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THE BALLISTIC USE OF A MOVING-COIL GALAVANOMETER IN MEASURING DISCHARGES OBEYING THE EXPONENTIAL DECAY LAW.

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Introduction.

In the ballistic use of galvanometers, it is generally assumed that the period of discharge must be negligible compared with the period of the galvanometer. That this assumption is not necessary does not seem to be well known.

Weber[1] seems to have first considered and obtained an approximate solution for the effect on galvanometer throws due to the duration of the rotation of an earth-inductor producing them. Chwolson[2] later considered in the multiplication and the recoil methods, the effects of errors in the timing of the successive throws. According to Dorn,[3] Chwolson's work was in error. Dorn himself developed approximation formulas for the effects of these two deviations from simple theory and verified them for the case of the sine discharge of the earth-inductor. Diesselhorst[4] revised in a simpler way the work of Dorn, and in addition considered for discharges of short duration the limits of error due to variations in the law of the unidirectional discharge, the correction factor for a constant current discharge, and the first order correction for a damped discharge. More recently Peirce,[5] in an excellent article, using a graphical method considered the effects of the duration of discharge for discharges of various types, and also deduced from theoretical considerations the correction factor to be applied to the galvanometer throws for certain simple types, among which was that obeying the

[1] Abh. der k. Sachs. Ges. d. Wiss., 1, p. 230, 1846.
[2] Melanges physiques et chimiques, St. Petersburg, p. 403, 1881.
[3] Ann. d. Phys., N. F., 17, p. 654, 1882.
[4] Ann. d. Phys., 4 F., 9, p. 712, 1902.
[5] Proc. of Am. Acad. of Arts and Sci., 44, p. 283, 1909.

exponential decay law. Unfortunately the papers of both Diesselhorst and Peirce are subject, as will be noted later, to a misinterpretation. Moreover the paper by Peirce, though it represents a distinct advance over previous work, is still incomplete.

Grassot[1] in connection with his fluxmeter described a method of measuring quantities of electricity which is practically independent of the duration or manner of passage. The same principle, that of a relatively very weak coil control, was used and the same practical results were obtained by Rohmann[2] in his second method of increasing the sensibility of a moving-coil galvanometer by means of large variations in the strength of the magnetic field containing the moving coil.

H. A. Wilson[3] considered the case of an undamped moving-coil galvanometer with a so-called radial field and concluded that, even though the time of passage of the transient current was not small compared with the galvanometer period, the deflections would be proportional to the quantities passing. The consideration of a steady current deflection shows the conclusion to be in error. Wenner,[4] considering the charging of a condenser through an undamped galvanometer, concluded that, within certain limits, the deflections were independent of the rate of charging.

The writer's special interest in this general subject of measuring discharges of considerable duration has resulted from an attempt to apply Corbino's[5] method in checking some results obtained on the thermal capacity of tungsten at incandescent temperatures. It was soon noted that the common assumption of a period of discharge negligible in comparison with the period of the galvanometer was far from the truth. In ignorance of the works of Dorn, Diesselhorst, and Peirce, it seemed to the writer that a definite correction factor, when once the law of discharge is known, should be obtainable. For the case of the exponentially decaying discharge, the one of immediate interest, such a simple factor has been found. A certain lack of definiteness and completeness, as already suggested, in the previous discussions of this case has led to the presentation of the following statement of theory and its test.

THEORY.

The equation of motion for a galvanometer coil traversed by a current I (see Table I.) and located centrally in a so-called radial field—that is

[1] Jour. de Phys., IV., 3, p. 696, 1904. See also Jones, Proc. of Phys. Soc. of Lond., 26, p. 80, 1914.

[2] Phys. Zeit., 14, p. 203, 1913.

[3] Phil. Mag., VI., 12, p. 269, 1906.

[4] PHYS. REV., 25, p. 139, 1907.

[5] Phys. Zeit., 13, p. 375, 1912.

TABLE I.

Symbols and Quantities.

I	Current traversing the galvanometer coil.
θ	Angular deflection of coil.
t	Time.
K	Moment of inertia of coil.
B	Damping factor for the coil on open circuit.
B_1	Damping factor for the coil on closed circuit.
D	Restoring couple per unit angular deflection due to the coil suspension.
G	Deflecting couple per unit of current traversing the coil.
E	Intrinsic E. M. F. in the circuit containing the coil.
r	Resistance of the circuit containing the coil.
L	Self inductance of the circuit containing the coil.
Q	Quantity of electricity discharged through the coil.
E_0	Initial value of E.
p	Inverse of the time-constant for the discharge through the coil.
$c_1, c_2, c_3, \beta_1, \beta_2, \gamma, \omega, p_1$	Constants defined by equations (9), (10), (11), (12), (28), (29) and (38).
θ_0	Maximum value of θ.
τ	Value of t corresponding to θ_0.
T	Period of galvanometer for an impulsive discharge.
λ	Logarithmic decrement of galvanometer for an impulsive discharge.
ϕ	Correction factor giving ratio of deflection for an impulsive discharge to the deflection for a prolonged discharge of the same quantity.
$(')$	Quantities referring to an impulsive closed circuit discharge as through the secondary of a mutual-inductance.
$('')$	Quantities referring to an impulsive open circuit discharge as from a condenser.

one in which for all ordinary deflections of the coil the torque due to a current is independent of the position of the coil—is given by

$$GI - K\frac{d^2\theta}{dt^2} - B\frac{d\theta}{dt} - D\theta = 0. \tag{1}$$

The successive terms represent torques due respectively to the current through the coil, the inertia of the moving system, the damping from other causes than the generator action of the coil, and the directing action of the suspension. Attention should here be directed to the fact that the damping effect due to the generator action of the coil is included in the torque GI, for the current I which actually flows is, on account of the generator action, less than that current which would flow in case there were no such action, that is in case the coil were held rigid. In other words, the damping effect due to the generator action is manifested by a reduced current, I. In general, neglecting capacity effects, an expression for I may be obtained by considering the E.M.F.'s of the galvanometer coil circuit, thus

$$E - L\frac{dI}{dt} - rI - G\frac{d\theta}{dt} = 0. \tag{2}$$

Therefore with a slight rearrangement we have

$$(3) \qquad \frac{d^2\theta}{dt^2} + \frac{B + G^2/r}{K}\frac{d\theta}{dt} + \frac{D}{K}\theta = \frac{G}{Kr}\left(E - L\frac{dI}{dt}\right).$$

As is well known no counter E.M.F. other than that indicated in (2) by rI can affect the total quantity of electricity discharged through the galvanometer, due account being taken of the sign of the discharge at various stages. Thus

$$(4) \quad Q = \int_0^\infty I\,dt = \int_0^\infty \frac{E}{r}dt - \frac{L}{r}\int_0^\infty \frac{dI}{dt}dt - \frac{G}{r}\int_0^\infty \frac{d\theta}{dt}dt = \int_0^\infty \frac{E}{r}dt,$$

that is, the total charge which passes depends on the E.M.F. and the resistance only. Differentiation of (1) with respect to time leads to an expression for dI/dt which may be substituted in (3). This gives

$$(5) \qquad \frac{d^3\theta}{dt^3} + \frac{LB + Kr}{LK}\frac{d^2\theta}{dt^2} + \frac{LD + G^2 + Br}{LK}\frac{d\theta}{dt} + \frac{Dr}{LK}\theta = \frac{G}{LK}E.$$

For our special problem it is necessary to define what is meant by a "discharge obeying the exponential decay law." The most practical definition requires that, for such a discharge, there be present in the circuit an intrinsic E.M.F. of the form

$$(6) \qquad E = E_0 e^{-pt}.$$

The discharge current, however, which exists in a galvanometer circuit, on account of the distorting effect of the generator action of the moving coil, will seldom be found to obey a similar law. In case the term $G(d\theta/dt)$ of (2) is sufficiently small comparatively, there is a close approach to it. This condition occurs commonly during a considerable portion of the discharge in case (6) is fulfilled, only when $1/p$ is large in comparison with the time of throw of the galvanometer. The treatment of such cases is not important since it has been long known that the galvanometer deflection then tends towards independence of the particular law of discharge and towards dependence only upon the quantity of electricity passing.

Our particular interest, however, is in measuring discharges where $1/p$ is of the order of the time of throw of the galvanometer, that is in obtaining by means of a correction factor the throw in case the whole quantity had passed in a very short period of time. In the process of carrying out this plan (5) may be actually solved subject to (6) by a method similar to that used below for the simpler case in which the self-inductance is neglected. Computation shows, as will be pointed out later, that for the writer's tests and also for most other probable tests such a procedure

is justifiable. With this assumption of a negligible self-inductance, there results from either (3) or (5)

$$\frac{d^2\theta}{dt^2} + \frac{B + G^2/r}{K}\frac{d\theta}{dt} + \frac{D}{K}\theta = \frac{GE_0}{Kr}e^{-pt}. \tag{7}$$

By means of (4), E_0/r may be replaced by Qp. (7) may then be written as

$$\frac{d^2\theta}{dt^2} + \frac{B_1}{K}\frac{d\theta}{dt} + \frac{D}{K}\theta = \frac{GQp}{K}e^{-pt}. \tag{8}$$

It is to be noticed by comparing (8) and (1) that when the self-inductance effect is negligible, the behavior of the coil when in a closed circuit containing an intrinsic E.M.F. obeying (6), is exactly the same as though it possessed a new damping coefficient B_1 instead of B and were traversed by a current rigidly obeying the exponential decay law. The misinterpretation liable to follow in considering the works of Diesselhorst and Peirce, as mentioned above, consists in relating B_1 to the actual current flowing through the galvanometer coil. If one considers theoretically the form of the current curve existing in a galvanometer circuit as it would exist but for the generator action of the coil, he is not liable to error. The case is quite different, however, if one determines with an oscillograph the actual current curve.

The complete solution of (8) is of the form

$$\theta = c_1e^{-\beta_1 t} + c_2e^{-\beta_2 t} + c_3e^{-pt}, \tag{9}$$

where

$$\beta_1 = \frac{1}{2K}(B_1 + \sqrt{B_1^2 - 4KD}), \tag{10}$$

$$\beta_2 = \frac{1}{2K}(B_1 - \sqrt{B_1^2 - 4KD}), \tag{11}$$

and

$$c_3 = \frac{GQp}{K(p - \beta_1)(p - \beta_2)}. \tag{12}$$

Introducing the natural boundary conditions

$$[\theta = 0]_{t=0} \quad \text{and} \quad \left[\frac{d\theta}{dt} = 0\right]_{t=0}, \tag{13}$$

gives

$$\frac{\theta}{c_3} = \frac{p - \beta_2}{\beta_2 - \beta_1}e^{-\beta_1 t} + \frac{p - \beta_1}{\beta_1 - \beta_2}e^{-\beta_2 t} + e^{-pt}. \tag{14}$$

Differentiation of (14) leads to

$$\frac{1}{pc_3}\frac{d\theta}{dt} = \frac{p - \beta_2}{\beta_1 - \beta_2} \times \frac{\beta_1}{p}e^{-\beta_1 t} + \frac{p - \beta_1}{\beta_2 - \beta_1} \times \frac{\beta_2}{p}e^{-\beta_2 t} - e^{-pt}. \tag{15}$$

To obtain an expression for the maximum angular deflection θ_0, at time τ, (14) and (15) may be combined subject to

$$\left[\frac{d\theta}{dt} = 0\right]_{t=\tau}. \tag{16}$$

We then have on substituting the value for c_3 from (12)

$$\theta_0 = \frac{GQ}{K(\beta_2 - \beta_1)}(e^{-\beta_1\tau} - e^{-\beta_2\tau}). \tag{17}$$

As is usual in similar cases dealing with a damped moving coil actuated by an impulsive discharge, we must consider three cases depending on whether the term $(B_1^2 - 4KD)$ common to the expressions for β_1 and β_2 is less than, equal to, or greater than zero.

Condition I. $(B_1^2 - 4KD) < 0$.

β_1 and β_2 are independent of the characteristics of the discharge, being thus the same as for the case of an impulsive discharge. A negative value of the radical part of β_1 and β_2 leads us to expect here as in the simpler case some sort of a damped vibrating action. In order to introduce the characteristics of the motion accompanying the impulsive discharge let us as in that simpler case write

$$\beta_1 = \frac{2}{T}(\lambda + \pi\sqrt{-1}) \tag{18}$$

and

$$\beta_2 = \frac{2}{T}(\lambda - \pi\sqrt{-1}). \tag{19}$$

T and λ represent respectively the period and the logarithmic decrement of the motion in the simpler case. Substitution of (18) and (19) in (17) gives

$$\theta_0 = \frac{GQT}{2\pi K} e^{-2\lambda(\tau/T)} \sin 2\pi \frac{\tau}{T}. \tag{20}$$

The value of τ is determined by applying condition (16) to (15). There results when β_1 and β_2 are eliminated,

$$e^{-[p-(2\lambda/T)]\tau} = \cos\frac{2\pi}{T}\tau + \frac{2\lambda^2 - \lambda pT + 2\pi^2}{\pi pT}\sin\frac{2\pi}{T}\tau. \tag{21}$$

Equations (20) and (21) serve to express the galvanometer throw θ_0 in terms of the charge Q, the characteristic discharge constant p, and the constant of the galvanometer for the case where the charge passes quickly. A similar expression for the case of an actual passage of a charge through the same circuit in a negligibly short time may be obtained from (20) and (21) by assuming p to be infinite. Representing these quantities by similar symbols primed, we have

$$\theta_0' = \frac{GQ'T}{2\pi K} e^{-2\lambda(\tau'/T)} \sin 2\pi \frac{\tau'}{T} \tag{22}$$

and

$$\tau' = \frac{T}{2\pi} \tan^{-1} \frac{\pi}{\lambda}. \tag{23}$$

The correction factor ϕ', the quantity by which the galvanometer throws must be multiplied in the case of the prolonged discharge to obtain the corresponding desired throws for the case of the impulsive discharge through the same circuit is evidently

$$\phi' = \left[\frac{\theta_0'}{\theta_0}\right]_{Q'=Q} = \frac{e^{-2\lambda(\tau'/T)}}{e^{-2\lambda(\tau/T)}} \times \frac{\sin 2\pi\left(\frac{\tau'}{T}\right)}{\sin 2\pi\left(\frac{\tau}{T}\right)}, \tag{24}$$

where τ and τ' are determined by (21) and (23). The determination of τ from (21) is not the formidable task that it appears at first sight. The assumption of different values for τ and the consequent evaluation of the left-hand term of (21) seems to be the easy method of operation. After the experience of one or two such determinations it will usually not be necessary to make more than two assumptions as to τ in order to evaulate it to the degree of accuracy warranted by the determinations of T and λ. Often the first approximation obtained by neglecting the left-hand member of (21) will suffice.

In the paper referred to by Peirce, a simple expression of the type (24) was not obtained. Nor does there seem, in following out his method, to be any simple means of arriving at any expression similar to (21) which may be used in determining τ.

In Fig. 1, there are represented for a particular case (No. 1, Table III.), as a function of the time, the relative positions of a galvanometer coil due to (A) an impulsive discharge and (B) an equal prolonged discharge. While various changes in the constants p, λ and T will shift these curves with respect to one another, their general shapes are characteristic for all discharges obeying (6). It is evident that $\tau > \tau'$ and that $\phi' > 1$.

In case one desires to compare the quantity of electricity which is discharged according to some particular decay law, with that discharged through the secondary coil of a mutual-inductance connected permanently in series with the galvanometer coil, (24) will suffice. However, if the comparison is to be made with the quantity discharged from a condenser, a somewhat different correction factor will be required. The latter discharge, assumed brief, represents an open circuit discharge for which B_1 in the previous development is to be replaced by B. Representing the

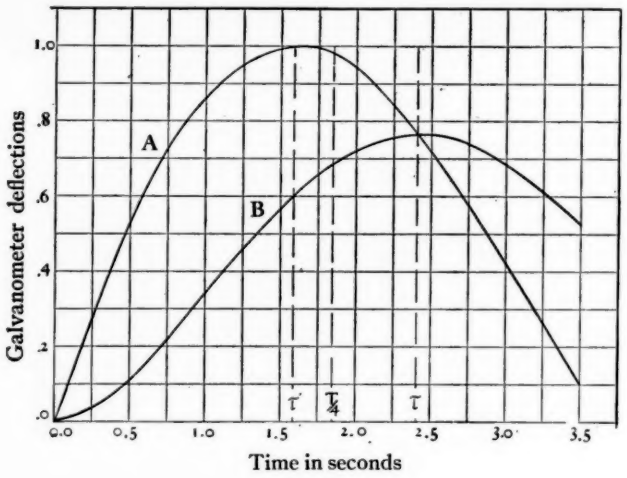

Fig. 1.

The deflections of a galvanometer on closed circuit as a function of time (A) for an impulsive discharge and (B) for a prolonged discharge of an equal quantity due to an intrinsic E. M. F. of the type $E = E_0 e^{-pt}$.

quantities entering here by double primed ($''$) symbols, we have as an equation analogous to (24)

$$(25) \qquad \phi'' = \left[\frac{\theta_0''}{\theta_0}\right]_{Q''=Q} = \frac{T''}{T} \frac{e^{-2\lambda''}\frac{\tau''}{T''}}{e^{-2\lambda}\frac{\tau}{T}} \frac{\sin 2\pi\frac{\tau''}{T''}}{\sin 2\pi\frac{\tau}{T}},$$

where τ is given by (21) and τ'' by

$$(26) \qquad \tau'' = \frac{T''}{2\pi}\tan^{-1}\frac{\pi}{\lambda''}.$$

T and T'' are related by a well-known expression derived from a comparison of $(B_1^2 - 4KD)$ with $(B^2 - 4KD)$, thus

$$(27) \qquad \frac{T''}{T} = \left(\frac{1 + \frac{\lambda''^2}{\pi^2}}{1 + \frac{\lambda^2}{\pi^2}}\right)^{1/2}.$$

This expression may be of considerable value in cases where it is difficult to obtain accurate determinations of T due to the periodic motion being heavily damped.

Condition II. $(B_1^2 - 4KD) > 0$.

Here represent β_1 and β_2 by

$$(28) \qquad \beta_1 = \gamma + \omega$$

and

$$\beta_2 = \gamma - \omega. \tag{29}$$

There results the expression analogous to (24),

$$\phi' = \left[\frac{\theta_0'}{\theta_0}\right]_{Q'=Q} = e^{-\gamma(\tau'-\tau)}\frac{\sinh \omega\tau'}{\sinh \omega\tau}, \tag{30}$$

where

$$e^{-(p-\gamma)\tau} = \cosh \omega\tau + \frac{\gamma^2 - \gamma p - \omega^2}{\omega p}\sinh \omega\tau \tag{31}$$

and

$$\tau' = \frac{1}{\omega}\tanh^{-1}\frac{\omega}{\gamma}. \tag{32}$$

Condition III. $(\beta_1^2 - 4KD) = 0.$

As a limiting case of condition II., there results

$$\phi' = \left[\frac{\theta_0'}{\theta_0}\right]_{Q'=Q} = e^{-\gamma(\tau'-\tau)}\frac{\tau'}{\tau}, \tag{33}$$

where

$$e^{-(p-\gamma)\tau} = 1 + \frac{\gamma^2 - \gamma p}{p}\tau \tag{34}$$

and

$$\tau' = \frac{1}{\gamma}. \tag{35}$$

Preliminary Galvanometer Tests.

Previous to considering the applicability of (24) and of (25) it is necessary (*a*) to consider the effects of neglecting the self-inductance in the galvanometer circuit, (*b*) to see if the fundamental assumption of a condition such that the torque due to a given current was independent of the galvanometer deflection throughout the range of deflections used was applicable, and (*c*) to see if there existed the peculiar condition of an apparent galvanometer resistance different from the true resistance as described by Peirce.[1]

As stated above, when there is a self-inductance in the galvanometer circuit, the equation of motion (5) can be solved. For the case of damped vibrations the equations are similar to those already given by (9) to (24), differing only from them owing to the introduction of another exponential term in the right-hand member of (9). For such an assumed case in which $\lambda = pT = \pi$, $r = 1{,}000$ ohms, and $L = 1$ henry, a case much worse than would be probable in practice particularly from the standpoint of the ratio r/L, the error due to neglecting the self-inductance was found

[1] Proc. Amer. Acad. of Arts and Sciences, 44, p. 63, 1908 (particularly pp. 79 and 80).

to be only 0.2 per cent. This conclusion as to the magnitude of the error was verified by measurements made with the secondary of a 0.3 kw. transformer in series with the galvanometer. No effect due to its self-inductance could be detected with certainty. These facts were taken as justifying the assumption made in passing from (5) to (7).

The fundamental assumption of a torque due to a given current, which is independent of the coil position throughout the range of deflections used, in other words the assumption that G is constant was tested by making determinations of λ at various times as the oscillations of the coil on closed and on open circuits died down. The constancy of G leads to the constancy of λ. Conversely constancy of λ, as may be shown, indicates the constancy of G. A somewhat more striking test however appears in connection with the third preliminary test.

This third test results from the indicated significance of the term B_1, in (8) thus

$$B_1 = B + G^2/r, \tag{36}$$

or

$$r = \frac{G^2}{B_1 - B} = \frac{G^2}{2K} \times \frac{2K}{B_1 - B}. \tag{37}$$

$2K/(B_1 - B)$ may be evaluated with the aid of (10), (11), (18) and (19). By platting $2K/(B_1 - B)$ as a function of r, Peirce, as noted above, found a relation of such a character as to indicate an apparent resistance for his galvanometer which was double the real resistance. The same test yielded for the galvanometer used by the writer results which are incorporated in Table II. Three conditions distinguished by different

TABLE II.

Data and Results for Third Preliminary Galvanometer Test.

Condition I.			Condition II.			Condition III.		
r Ohms.	λ	$\frac{2K}{B_1-B}$	r Ohms.	λ	$\frac{2K}{B_1-B}$	r Ohms.	λ	$\frac{2K}{B_1-B}$
∞	0.013	∞	∞	0.019	∞	∞	0.0139	∞
20,510	.148	15.50	1,310	.509	16.25	3,010	.1275	135.0
10,510	.282	7.81	1,110	.603	13.70	2,010	.1842	90.2
5,510	.529	4.108	910	0.735	11.29	1,310	.2756	58.8
3,010	0.988	2.250	710	1.013	8.30	910	.3935	40.7
2,510	1.216	1.860	610	1.112	7.63	710	.5040	31.7
1,510	2.330	1.125	510	1.370	6.34	510	.7000	22.9
$T_{r=\infty}$ = 4.18 sec.			$T_{r=\infty}$ = 15.7 sec.			$T_{r=\infty}$ = 30.6 sec.		

The galvanometer resistance of 510 ohms differs from that given in Table III due to a short circuiting of some of the turns of wire in the coil.

moments of inertia of the syspended system were made use of. Plats of these indicate that G is a constant and that the apparent resistance of the galvanometer, contrary to what was found by Peirce, is the same as the true resistance.

As another preliminary test, the accuracy with which (6) was satisfied experimentally was examined. Due to self-inductance in electric circuits a rigid fulfillment of (6) is not to be expected. In the arrangement of apparatus (Fig. 2) used in the experimental verification of (24), the self-inductance of the heating circuit leads to an expression of the type

$$E = E_0(e^{-pt} - e^{-p_1 t}) \tag{38}$$

for the intrinsic E.M.F. instead of (6). Measurements with a known self-inductance introduced in various places showed that the time-constant $1/p_1$ must be negligible in comparison with $1/p$. Hence, experimentally (6) was shown to be applicable.

EXPERIMENTAL VERIFICATION OF (24).

The galvanometer used was a type H instrument made by the Leeds and Northrup Co. The deflections were indicated by the movements of the image of a short, straight, thin tungsten filament on a screen from 4 to 7 meters distant from the galvanometer mirror. Due to the deflections of the galvanometer being alternately in opposite directions, it was impossible to take the precautions noted by Zeleny[1] against changes of set in the suspension. It was often noted, however, that this effect was small, certainly not as great as the deviations in the observed throws.

The method used in testing (24) is based on a slight modification of Corbino's method[2] of measuring the thermal capacity of a small, electrically conducting filament at high temperatures in an evacuated chamber. The writer's arrangement which will be discussed more fully in a forthcoming paper on the thermal capacities of tungsten and carbon, is indicated in Fig. 2. In order to eliminate the disturbance arising from the cooled portions of the filament $R + R'$ in one branch of the bridge as in Corbino's method, another filament R' of the same diameter but of shorter length than the filament $R + R'$ is introduced in the other branch in series with it. The two branches xx are made equal to one another. In effect for the purposes at hand, we have then in the bridge a single lamp filament R of uniform temperature throughout. Corbino has shown that, if the bridge has been balanced for steady currents first when the key k is closed and then secondly, by shifting only the contact c, when the key k is opened, there is a varying potential difference between the terminals of the galvanometer branch immediately following the

[1] PHYS. REV., 23, p. 399, 1906.

[2] Phys. Zeit., 13, p. 375, 1912.

opening or closing of k, which is of the exponentially decaying type. In his work, he concluded that the discharges were so nearly impulsive as

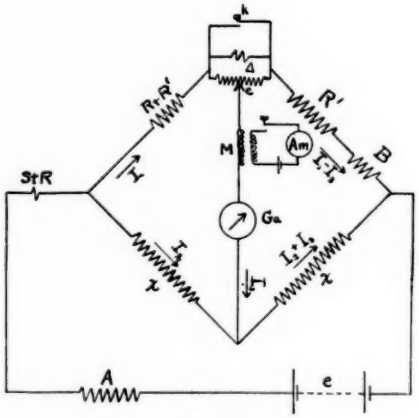

Fig. 2.
Arrangement of apparatus for testing (24).

to justify that assumption. This is not the case, however, with filaments of comparatively large cross-sections such as the writer has used. In some instances which have occurred the time-constants of the decaying discharges have been greater than the periods of the galvanometer. Data obtained even under such conditions were found to be very consistent when corrected according to (24) or to (25). Unfortunately where this condition prevails, an accurate determination of p by Corbino's method

TABLE III.

Test of (24) *for a Discharge Through a Galvanometer Due to an Intrinsic E.M.F. of the Type* $E = E_0 e^{-pt}$ *Where the Time-Constant* $1/p$ (*Fig.* 2) *is Equal to* 1.06 *sec.*

r Ohms.	T Sec.	λ	θ_0' Div.	$\frac{\theta_0}{Q}$ Div. / Micro-coulomb	$\frac{Q'}{\phi'}$ Micro-coulombs.	ϕ'	Q' Micro-coulombs.	$Q'r$ Micro-volts × Sec.	e^{-pT}
10,540	7.35	0.692	9.07	20.08	0.452	1.296	0.586	6,180	0.103
5,280[1]	8.70	2.138	5.54	6.28	0.882	1.322	1.167	6,160	.115
15,540	4.30	1.355	7.29	32.45	0.225	1.680	0.378	5,870	.249
5,540	21.5	0.166	5.04	4.75	1.060	1.048	1.112	6,160	.0026
5,280[1]	21.5	0.354	2.17	1.955	1.110	1.047	1.162	6,140	.0033
5,540	15.3	0.234	6.56	6.38	1.030	1.088	1.120	6,210	.0125
5,280[1]	15.4	0.491	2.77	2.580	1.074	1.091	1.172	6,190	.0145
5,540	11.6	0.360	9.54	9.77	0.976	1.145	1.118	6,200	.032
5,280[1]	11.8	0.812	3.72	3.69	1.009	1.150	1.160	6,120	.038

[1] For these sets the galvanometer whose resistance was 480 ohms was shunted with a 400 ohm resistance.

is very difficult. Other conditions less extreme have been selected, therefore, for the test of the foregoing theory. Certain data and results for such a test arranged in the order in which the data were taken, are incorporated in Table III. The various sets indicated were obtained essentially by varying the moment of inertia of the moving coil or by shunting it with a known resistance. The former method was carried out by adjusting two lead cubes that could be fastened at various positions on an aluminum rod which itself was attached to the bottom of the coil. In applying the above theory to cases where the method of shunting was employed, the galvanometer and shunt combination may be treated as a new galvanometer. It will be seen by the application of (20) and (21) or of (22) and (23), that the ratios of the deflections as given for the galvanometer when shunted and when unshunted for otherwise like conditions, are very closely as expected. Throughout the test the two steady current temperatures of the lamps, excepting for negligibly small changes due to the variations in x, were maintained constant. Consequently on opening and closing the switch k, the same quantity of electricity was in all cases discharged through the galvanometer circuit. The time-constant of this discharge $1/p$ according to Corbino's method was found to be 1.06 sec. The agreement indicated in the column of the table headed $Q'r$ is very good if one excepts the third set. Here the large value of λ and the shortness of the period made the direct determination of T, which was used, difficult. Had a method employing (27) been used, judging from later data obtained in other instances, there would not have been even this single exception. The constancy of the values for $Q'r$ indicate the verification of (24). As interesting data, there have been included in the last column of the table the relative values of the intrinsic E.M.F. at the times τ of the corresponding maximum elongations, and thus incidentally also, for the case of a galvanometer coil held motionless, the fractional parts of the total quantities of electricity discharged which remain at the times τ.

With (24) once checked, checking (25) may consist merely in verifying well-known relations for the ratios of the throws produced by condenser discharges to those produced by discharges from the secondary of a mutual inductance in series with the galvanometer. The writer, however, has tested (25) directly and has found the expected agreement.

THE DETERMINATION OF THE TIME-CONSTANT FOR A DISCHARGE OBEYING (6).

With the occurrence of a time-constant of the order of the galvanometer period, as was noted in the preceding subdivision, difficulty

was experienced in obtaining p by Corbino's method. In such a case, a slight extension of the theory already given will suffice for its determination. Q' may then be found in the manner already indicated.

For this purpose, it is necessary that data similar to that indicated above shall be taken with at least two galvanometers of quite different periods. Different values of p must then be assumed and the corresponding values of $Q'r$ determined. That value of p which leads to a common value for $Q'r$ is the value sought. In general the greater the difference between the two values of ϕ' or of ϕ'' for a set, the greater the accuracy with which p may be determined. In illustration of this method, the data given in Table III. may be used. The data obtained in connection with tests 1, 2, 4 and 5 for two assumed values of $1/p$ lead to the values of $Q'r$ indicated in Table IV.

TABLE IV.

The Determination of p (Supposed Unknown) from Data Given in Table III.

Test.	$\frac{1}{p}$ (Assumed), Sec.	$Q'r$ Microvolts × Sec.	Tests Combined.	$\frac{1}{p}$ (Computed), Sec.
1	1.06	6,180	1 and 4	1.068
	1.10	6,080	1 and 5	1.078
2	1.06	6,160	2 and 4	1.060
	1.10	6,100	2 and 5	1.080
4	1.06	6,160		Av... 1.072
	1.10	6,140		
5	1.06	6,140		
	1.10	6,110		

As has been justified by repeated computations for small intervals, the relation between $Q'r$ and $1/p$ has been assumed to be linear for the interval 1.06 sec. to 1.10 sec. The computed values of the last column may therefore be readily obtained by noting the points of crossing of the straight lines on a plat of $Q'r$ as a function of $1/p$. The average value of $1/p$ thus obtained is 1.072 sec. This agrees extremely well with 1.06 sec. which was obtained by Corbino's method. In Table V., there are given the necessary data, computations and results for a discharge for which no satisfactory value of p could be obtained with the equipment at hand using Corbino's method. A slightly different method as to details is here indicated. For the writer's purpose, as will be noted in a later paper, the accuracy of this determination of p was quite satisfactory.

In order to decide whether (6) is fulfilled or not, several sets of data with galvanometers of different periods will be necessary. If a single assumed value of p leads to a common value for $Q'R$, whatever the period

TABLE V.

Data and Computations for the Determination of p for a Case where Corbino's Method was Difficult of Application.

r Ohms.	λ''	λ	T Sec.	θ_0 Div.	$\frac{\theta_0''}{Q''}$ Div. / Micro-coulomb.	ϕ''		$Q'r$ Microvolts × Sec.		
						$p = 0.18$ / Sec.	$p = 0.17$ / Sec.	$p = 0.18$ / Sec.	$p = 0.17$ / Sec.	$p = 0.172$ / Sec.
3,060	0.014	0.137	32.4	7.46	8.38	1.445	1.481	3,930	4,030	4,010
3,060	.016	.194	22.8	9.09	12.21	1.727	1.770	3,920	4,020	4,000
3,060	.018	.468	8.83	11.02	29.5	3.44	3.59	3,930	4,110	4,070
5,560	.018	.265	8.78	6.52	29.5	3.14	3.28	3,860	4,030	4,000
5,560	.013	.540	4.37	7.22	63.8	6.12	6.48	3,850	4,080	4,030
									Av.....	4,020

of the galvanometer, (6) is fulfilled and vice versa. Thus the columns headed $Q'r$ of Tables III. and V. verify Corbino's theoretical conclusion as to the occurrence in his method of an E.M.F. obeying (6).

SUMMARY.

1. Expressions simpler and more complete than previous ones have been developed for obtaining ϕ' and ϕ'', the ratios of the deflections due to impulse discharges through a galvanometer on closed and on open circuits respectively to that produced by a prolonged discharge of an equal quantity due to an intrinsic E.M.F. obeying the exponential decay law.

2. The effect of self-inductance in the galvanometer circuit on the throws under all ordinary conditions is negligible.

3. The apparent resistance of the writer's galvanometer when used ballistically has been found to agree exactly with its real resistance, contrary to what was found by Peirce.

4. The expressions developed for ϕ' and ϕ'' have been experimentally verified, using a slight modification of Corbino's method of measuring the thermal capacity of filaments at high temperatures.

5. A method has been devised and applied for determining the time-constant of a discharge known to be of the exponentially decaying type.

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March, 1915.

ELECTRIC DOUBLE REFRACTION IN LIQUIDS.

BY HAROLD E. McCOMB.

THE velocity of light, vibrating in different planes in di-electric media, subjected to electric strain, was first investigated by Kerr[1] in 1894. After experimenting upon a number of liquids he concluded that the velocity of the component vibration polarized perpendicular to the lines of force was changed.

Later, G. Aeckerlein,[2] following a method similar to that used by Kerr, investigated the above effect in nitro-benzol and nitro-toluol. He found that in the former the perpendicular component is accelerated and the parallel component retarded, the ratio being about 2 : 1.

In the present investigation an attempt has been made to measure accurately the effect on each component.

APPARATUS.

The apparatus consisted of a Michelson interferometer mounted on a cement block. In the paths A and B were placed tubes of the liquid to be investigated. The tubes were ground so that they were practically the same length (22 cm.) and the ends covered with interferometer plates of the same optical thickness. The electrodes (made of brass) were placed within the tubes and held apart by glass plates of definite thickness. By placing the faces of the electrodes in one tube parallel to the plane of the table and in the other tube perpendicular to this plane the effect on either component could be measured without rotating the nicol. Later it was found more convenient to rotate the nicol and adjust all electrodes perpendicular to the table. The nicol N was arranged so that it could be quickly and accurately rotated 90 degrees, first transmitting light vibrating parallel to the table and then perpendicular. It was thus a simple matter to study the effect on each component in succession in the same tube. A direct-vision spectroscope was placed at S and a telescope at T. The total reflecting prism P was used to direct the light to the telescope T when adjustments were being made with sodium bands. All of the optical part of the apparatus except the light

[1] J. G. Kerr, Phil. Mag., 37, 1894, p. 380.

[2] G. Aeckerlein, Physikalische Zeitschrift, 7, No. 17, p. 594.

sources, the spectroscope, and the telescope was enclosed in a glass case in order to eliminate sudden changes in temperature and air currents.

Electrical Apparatus.

The potentials were supplied from a storage battery (1,000 volts) in series with three 1,200-volt generators and were measured by a Weston voltmeter (V) with multipliers giving ranges (0–150), (0–300), etc., to (0–6000). The arrangement of the commutator (described later) is shown at C.

Experimental.

The apparatus was first carefully adjusted for sodium bands using the prism P and the telescope T. The prism was then removed and the Nernst light L gave a clear channeled spectrum in the spectroscope. The tubes were then interposed and brought directly in line with the beams of light A and B. This step was the most difficult in the whole operation and was almost impossible to carry out without the use of small diaphragms. After adjusting the tubes so that the two fields of

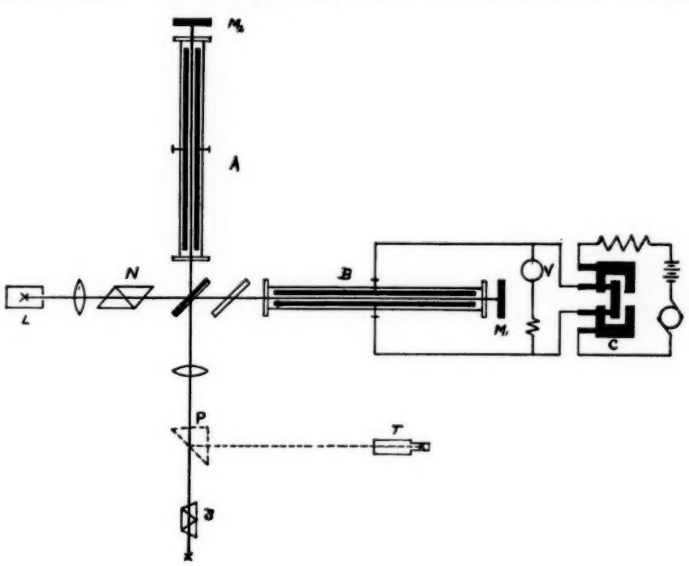

Fig. 1.

view were superimposed the air path A was increased or decreased by moving the mirror M_2 until the bands appeared. By applying the electric strain it was found that the bands usually appeared more quickly than when the liquids were simply allowed to stand. By applying the potential a distinct shifting of the bands was apparent, the amount depending upon the potential used. An attempt was made to measure accurately

the shift produced by the application and quick removal of a definite potential. For this purpose the spectroscope was fitted with an eye-piece having movable and stationary cross-hairs. This method might have proved satisfactory had the field of view remained stationary but owing to the heating effect the whole field of view continually shifted. Nevertheless measurements were made until a potential was applied which gave a shift of *one band*. Up to this point the shift was quite large and measurable but for exactly *one band shift* the field of view apparently remained stationary. This might have been predicted because an instant shift of exactly one band could not be detected by the eye. A device was then made for rapidly and uniformly making and breaking the circuit. It consisted of a large commutator highly insulated which could be rotated at speeds varying from a few R.P.M. up to several hundred. It was found that a speed of about 200 R.P.M. was most satisfactory, there being one make and one break for each revolution. The field of view in the spectroscope was diaphragmed down so that different colors could be investigated. To obtain the retardation, then, for any wave-length it was only necessary to observe the potential required to produce a shift of one or more bands. Shifts up to three bands were thus measured with considerable accuracy. The results with nitro benzol are given in the tables which follow. In the first table the first column gives the wave-length; the second column, the potential difference (electrostatic) required to give an acceleration of one wave-length on the perpendicular component; the third column, the values of "$B_\perp$" (perpendicular component) computed from Kerr's law,

$$B = \frac{\delta a^2}{V^2 l},$$

in which δ is the retardation or acceleration, a the distance between the electrodes, l their length, and V the potential. The fourth column gives the potential difference required to give a retardation of one wave-length on the parallel component; the fifth column, the value of $B_\parallel$ (parallel component); and the last column the ratio $B_\perp$ to $B_\parallel$.

The second table gives the same for δ = two wave-lengths retardation and acceleration.

With nitro-benzol, *the component vibrating parallel to the lines of force is retarded amd the perpendicular component is accelerated, the ratio being 0.53.*

Several other liquids were investigated but none gave as satisfactory results as were obtained with nitro-benzol. In most cases the effects were too small to be measured accurately and distortions in the field of

Nitro Benzol.

(One Wave-length Retardation.)

March 20, 1914. Temperature 20° C.

Wave-length $\mu\mu$.	Potential Difference Electrostatic.	$B_\perp$	Potential Difference Electrostatic.	$B_\parallel$	Ratio $B_\perp/B_\parallel$
660	8.24	$87.\times10^{-7}$	5.96	$167.\times10^{-7}$	.52
620	7.88	95.	5.85	173.	.55
580	7.57	103.	5.39	204.	.51
540	7.15	116.	5.22	218.	.53
660	8.17	89.	5.95	167.	.53
				Mean.....	.53

Nitro Benzol.

(Two Wave-lengths Retardation.)

Wave-length $\mu\mu$.	Potential Difference Electrostatic.	$B_\perp$	Potential Difference Electrostatic.	$B_\parallel$	Ratio $B_\perp/B_\parallel$
660	11.58	$88.\times10^{-7}$	8.46	$166.\times10^{-7}$	.53
620	11.21	94.	8.10	181.	.52
580	10.83	101.	7.81	194.	.52
540	10.17	115.	7.28	224.	.51
660	11.60	88.	8.48	165.	.53
				Mean.....	.53

Note.—Length of electrodes, 20 cm. (effective path 40 cm.). Distance between electrodes, .154 cm.

view caused considerable trouble. Carbon bi-sulphide and chloroform could be easily investigated with longer tubes or higher potentials but the effect is too small on either to give one band shift with the apparatus described here. The following qualitative measurements were made:

With Carbon Bi-sulphide.—Potentials were supplied from a static machine and measured approximately by means of a spark gap. By allowing the condensers to charge and discharge rapidly the effect was similar to that obtained with the commutator. Using this method no effect was observed upon the component vibrating perpendicular to the lines of force up to a 4 mm. spark gap potential. The other component, that is, the component vibrating parallel to the lines of force, is retarded and apparently is the only component affected.

With Chloroform.—Both components are accelerated, the component vibrating parallel to the lines of force is the larger.

In conclusion the writer wishes to acknowledge his indebtedness to Dr. C. A. Skinner for help and inspiration received during this work.

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THE RELATION BETWEEN THE ALPHA-RAY ACTIVITIES AND RANGES OF RADIUM AND ITS SHORT-LIVED PRODUCTS.

BY HERBERT N. McCOY AND EDWIN D. LEMAN.

IN a recent paper[1] it has been shown that the ratio between the α-ray activity of radioactinium and that of its products is in good agreement with the value calculated from the equation $I = kR$, where I is the ionization current in air due to a single α-particle, R is the range of the α-particle, and k is a constant for α-particles of all ranges.[2] McCoy and Viol[3] had previously shown that the relative α-ray activities in the thorium series, as calculated from the same equation, are in good accord with the experimental values. In this paper we wish to show that the relative activities of radium and its short-lived products are also in good agreement with those calculated from the known ranges.

The latest available data on the radium series[4] which we shall use in this paper are given in Table I.

TABLE I.

The Radium Series.

	Symbols.	Period.	Rays.	Ranges, Cm. at 15° C.
Radium.....	Ra	1730 years	α, β	3.30
Emanation.....	Em	3.85 days	α	4.16
Radium A.....	RaA	3.00 min.	α	4.75
Radium B.....	RaB	26.7 "	β	
Radium C_1.....	RaC_1	19.5 "	$\alpha(?), \beta$	
Radium C_2.....	RaC_2	1.4 "	β	
Radium C'.....	RaC'	10^{-6} sec. (?)	α	6.94

The accepted scheme of disintegration in this series, according to Fajans[5] is as follows:

[1] McCoy and Leman, PHYS. REV., *4*, 409 (1914).

[2] Geiger, Proc. Royal Soc., A, *82*, 486 (1909); A, 83, 505 (1910). Taylor, Phi . Mag., *21*, 571 (1911); *26*, 402 (1913).

[3] McCoy, PHYS. REV., *1*, 393 (1913).

[4] Kolowrat, Le Radium, *11*, 1 (1914).

[5] Phys. Zeit., *13*, 699 (1912).

$$\mathrm{Ra} \underset{\alpha,\beta}{\rightarrow} \mathrm{Em} \underset{\alpha}{\rightarrow} \mathrm{Ra}A \underset{\alpha}{\rightarrow} \mathrm{Ra}B \underset{\beta}{\rightarrow} \mathrm{Ra}C_1 \begin{cases} \overset{\alpha}{\nearrow} \mathrm{Ra}C_2 \overset{\beta}{\rightarrow} ? \\ \underset{\beta}{\searrow} \mathrm{Ra}C' \underset{\alpha}{\rightarrow} \mathrm{Ra}D \underset{\beta}{\rightarrow} \mathrm{Ra}E \underset{\beta}{\rightarrow} \mathrm{Ra}F \underset{\alpha}{\rightarrow} \end{cases}$$

According to this view, the product formerly called radium *C* is complex: C_1, which is the product of *B*, disintegrates in two ways; the first (principal) with the production of a β-particle giving C'; the second (subordinate) with the expulsion of an α-particle, giving C_2. The product C' also gives α-rays, and of every 10,000 α-particles produced by the *C* components, all but three are due to the change of C' into *D*, the balance being due to the change of C_1 into C_2.[1] If we assume that these conclusions are essentially correct, we see that the effect on the activity caused by a minute fraction of the α-particles of radium *C* having a different range from those of the main fraction, would be negligibly small. We shall, therefore, neglect the complexity of *C* in the discussions in this paper, merely pointing out that the present work furnishes no data regarding this important question.

The method of determining the relative α-ray activities of Ra and its short-lived products consisted in preparing a Ra-$BaSO_4$ film free from all of the subsequent products of Ra, and measuring its initial and final activities. The activities of such films increased for about six weeks after the preparation of the film and then remained practically constant during several months of observation, the constant activity in each case being taken as the final. The Ra-$BaSO_4$ film, free from its subsequent products, was prepared in the following manner: One c.c. of a solution of pure radium chloride in dilute hydrochloric acid was diluted to 10 c.c.; the solution was heated to its boiling point and a current of air bubbled through it for thirty minutes, the solution being kept near its boiling point and a few c.c. of water being added from time to time to replace that lost by evaporation. This procedure kept the solution free from emanation, and allowed Ra*A* to decay practically completely. A few drops of lead acetate solution were then added and hydrogen sulphide passed in. The lead sulphide, which was precipitated, removed *B*, *C*, *D*, *E*, and *F*. The precipitate was rapidly filtered off, and a current of air again bubbled through the filtrate, for ten minutes, keeping it near its boiling point and the volume constant. Lead sulphide was again precipitated in the solution, the precipitate filtered off, and the filtrate again treated in the manner just described, making a total of three precipitations of lead sulphide, and removing practically every trace of the products of radium. The various operations to this point had taken about fifty minutes. The filtrate from the last treatment

[1] Fajans, loc. cit.

was put into a 15 c.c. centrifuge tube, one c.c. of $N/100$ barium chloride solution added, then a few drops of dilute sulphuric acid. The solution was well shaken, and then centrifuged. The supernatant solution was decanted from the precipitate, and the latter was well washed, by decantation, with water acidified with a few drops of HCl, and finally with alcohol. A small portion of this precipitate was spread as uniformly as possible, with the aid of a glass rod and a little alcohol, over a flat polished brass plate, about 7 cm. in diameter. When the alcohol had evaporated, the less firmly adhering particles were brushed off, care being taken to guard the edges and back of the plate from radioactive contamination. The films so prepared were so thin as to be almost invisible; the differential absorption of α rays in such films was therefore negligibly small.

The time of precipitation of the sulphate was taken as zero time, as at this moment the precipitate was free from all of the subsequent products of radium. That the above method completely freed the radium from all of its active products was shown both by control experiments[1] and by the fact that the activity increased at a regular rate from the start. About thirty minutes elapsed between the time when the sulphates were precipitated and the time of making the first measurements. The activity measurements were made in a gold-leaf electroscope as previously described,[2] the active films being placed 7 cm. below the charged electrode, thus allowing all rays to reach their full ranges. Sufficient potential (about 600 volts) was used to insure practically complete saturation currents for the weak ionization produced. All activities were measured in comparison with a standard film of uranium oxide, the activities given being in terms of this standard. All measurements were made with the greatest care, and corrections were made for the accurately determined natural leak, which in every case was less than one per cent. of the standard. The initial activity of each film was less than, the final activity greater than, the standard. The activity increased nearly linearly for the first six hours so that by a small extrapolation the activity at time zero could be determined with a high degree of accuracy. The activities in terms of the standard are given in Table II. for two films.

TABLE II.

The Initial and Final Activities of Radium (Uncorrected).

Film.	Initial Activity I_0.	Final Activity I.	Ratio Uncorrected.
1	0.858	4.325	5.043
2	0.558	2.832	5.075

[1] Compare the work of McCoy and Viol, loc. cit., on the separation of Th-*B-C-D* from Th*X*.

[2] McCoy and Ashman, Am. Jour. Sci., *26*, 521 (1908).

But these results are subject to three corre ctions, viz.: the activity due to the β-rays, the escape of emanation from the film either by diffusion or by recoil, and the loss of other products by recoil.

The activity due to β-rays was determined by placing consecutive layers of aluminium foil over the Ra-$BaSO_4$ film, the first layer being of sufficient thickness to absorb all α-rays, and measuring the activity with each additional layer in the same electroscope as was used for the α-ray measurements. By plotting the activities against the thickness of the covering, and extrapolating to the axis of the activities, the β-ray activity could be ascertained with a fair degree of accuracy. This activity must be subtracted from the final activity of the film.

Since Kolowrat has shown that[1] the β-ray activity of radium free from its products is only 2 per cent. of the β-ray activity of radium in equilibrium with its short-lived products, and since the β-ray activity of the latter as measured in our electroscope was only about 0.5 per cent. of the α-ray activity, it follows that it is not necessary to apply any correction for β-ray activity of the radium itself.

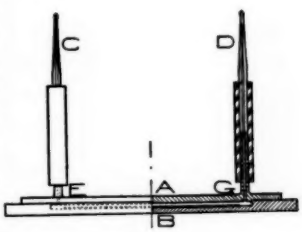

Fig. 1.

The amount of emanation lost by the film was determined by the use of a circular brass box as shown in Fig. 1. The cover, A, fitted with two small bore tubes E and G, was ground so as to fit very tightly over the lower compartment B. In the lower compartment was a recess about 0.2 cm. in depth and 8 cm. in diameter. Small bore glass tubes drawn out at one end, C and D, were attached to the tubes E and G by means of short pieces of thick-walled rubber tubing. The Ra-$BaSO_4$ film was placed in B, the cover A fitted on, and all joints sealed with wax. The ends of C and D were then sealed by fusion. After an interval of 40 days or more, the emanation which had accumulated was drawn into an emanation electroscope by a stream of air, care being taken to prevent any loss of the accumulated emanation and also to prevent any diminution of pressure within the box which might withdraw some of the Em from the film. The rate of discharge of the electroscope was measured, after the emanation had stood in it for three hours.

In order to find what fraction this quantity of Em was of the equilibrium quantity in the Ra-$BaSO_4$ film, two additional determinations were necessary. One c.c. of the original radium solution was diluted and then freed from subsequent active products as described in a preceding paragraph. By means of a small weight-pipette, an accurately

[1] Le Radium, 7, 269 (1910).

weighed portion of this solution was taken and uniformly distributed over the surface of a flat platinum plate, and evaporated to dryness. The activity of the residue, which was entirely invisible, was measured within twenty minutes, and the measurements extended over a short interval in order to be able to get the initial activity by extrapolation. To find the activity of the emanation from this quantity of radium, a known portion of the solution in the weight-pipette was run into a small round-bottom flask containing about 10 c.c. of dilute hydrochloric acid. The flask was well stopped with a two-hole rubber stopper fitted with delivering tubes, one of which extended into the solution. A current of air was bubbled through the solution for 30 minutes to drive off the accumulated emanation, and the flask then sealed by fusing the ends of the delivery tubes. After an interval of a few days, the emanation was drawn into the emanation electroscope, by allowing air to bubble through the solution which was heated near its boiling point. After three hours, the rate of discharge of the electroscope was measured.

The corrections for loss of emanation by the film were made as follows:

Initial activity of film No. 1	0.858
Initial activity of Ra on the platinum plate	.660

The radium on the platinum plate was obtained from 1.4942 gm. of solution. 1.5738 g. of the same solution gave after three days, 21.5 hours, a quantity of Em which discharged the electroscope in 46.45 seconds. Since for three days 21.5 hours, $1 - e^{-\lambda t} = 0.5036$, the equilibrium amount of Em from the solution would have discharged the electroscope in $0.5036 \times 46.45 = 23.40$ sec. Therefore the equilibrium amount of Em from 1.4942 gm. of this solution would discharge the electroscope in 24.64 sec. That is, a radium film, free from all subsequent products of radium, having an initial α-ray activity of 0.660 produces an equilibrium quantity of emanation which discharges the emanation electroscope in 24.64 sec. It then follows that the equilibrium quantity of emanation from film No. 1, which has an initial activity of 0.858 would discharge the emanation electroscope in 18.97 sec. The emanation which had escaped from film No. 1, when the latter had been sealed up 40 days or more, discharged the emanation electroscope in 1,748 seconds, therefore 1.08 per cent. of the equilibrium quantity of Em escaped from the film. This means that the quantity of emanation and the short-lived products in the film is 1.08 per cent. too low. In this film, the activity of the subsequent products of Ra is $4.297 - 0.858 = 3.439$, which value is 1.08 per cent. too low, hence the true activity of the products, if no Em had escaped, would be 3.476.

To find the loss of activity due to recoil, a polished brass plate 7 cm.

in diameter was placed 1 mm. above and completely insulated from film No. 1. A potential of 110 volts was maintained for six weeks, the upper plate being kept negatively charged. The activity of the plate was measured as quickly as possible after removing the potential, four minutes elapsing from the time the potential was removed to the mean time of making the measurements. The activity of the active matter which collected on the plate was 0.0374. Assuming that the active matter on the plate at the instant the potential was removed was Ra*A*, Ra*B*, and Ra*C* in equilibrium, the activity of the matter on this plate four minutes after the potential is removed is approximately 70 per cent. of its initial value.[1] Therefore the initial activity of the matter on the plate was 0.0534. To find what quantity of the matter on the plate is due to active deposit from escaped emanation and what quantity is due to direct recoil, it is necessary to recall that the emanation lost by this film was 1.08 per cent. of the equilibrium quantity, or the activity of the products, Em, Ra*A* and Ra*C*, lost was 0.037. Assuming that the activities are proportional to the 2/3 powers of the ranges, the fraction of the activity due to Ra*A* + Ra*C* is 65 per cent. of the total activity due to Em + Ra*A* + Ra*C*, or 0.0241 and that due to recoil is .0534 − .0241 = .0293.[2]

Table III. gives the results of two determinations. The final activity is corrected for β-ray activity, loss of emanation, and loss by recoil, these corrections being determined separately for each film:

TABLE III.

The Initial and Final Activities of Ra (Corrected).

Film.	Initial Activity I_0.	Final Activity I.	$\frac{I_0}{I}$.
1	0.858	4.363	5.085
2	0.558	2.863	5.133
			Mean . . 5.109

[1] Rutherford, Radioactive Substances and their Radiations (1913), page 491.

[2] It must be pointed out that this value is calculated on the assumption that at the instant the potential is removed, the active matter on the plate is Ra*A* + Ra*B* + Ra*C* in equilibrium, and there is a decided drop in activity before the first measurement is made, due to the rapid decay of Ra*A*. In the case of the active matter due to active deposit we do have this equilibrium, but in the case of recoil atoms, there is in all probability an excess of Ra*C* atoms, over the equilibrium number of Ra*A* atoms. This would mean that the percentage of the activity which decayed during the interval between the time the potential was removed and the time of measurement would not be so great as that calculated upon complete equilibrium, and the value of the loss by recoil would be even less than that calculated above. However, the loss by recoil is so small, that the value calculated above is certainly correct within experimental error, and it represents the maximum value.

In the series Ra-Em-RaA-RaC it is very probable that each member when present in equilibrium amount produces the same number of α-particles per unit time, if this is so, the equation

$$I = kR^{\frac{3}{2}}$$

leads to the theoretical results shown in Table IV.

TABLE IV.

	Ranges at 15°.	$R^{2/3}$.	Relative Activities.	
			Calculated.	Found.
Ra.....	3.30	2.217	1.00	[1.00]
Em.....	4.16	2.586	1.17	
RaA.....	4.75	2.826	1.28 } 4.09	4.11
RaC.....	6.94	3.639	1.64	

The only previous determination of the relative activities of radium and its products was made by Boltwood.[1] In these experiments the films were made by the evaporation of a chloride solution. Since such films gave off very large fractions of the emanation produced (in one case as high as 65 per cent.) it is not surprising that the results obtained were not very accurate. Instead of a ratio of 4.11 as found by us (last column, Table IV.) Boltwood found 4.65. For several years this result was looked upon as satisfactory,[2] since it was in good agreement with that calculated upon the assumption that the number of ions produced by an α-particle is proportional to the first power of its range[3] instead of the two-thirds power.

The good agreement of our results with the theoretical value as calcu-

TABLE V.

Relative Alpha-Ray Activities.

Ratios Measured.	Found.	Calculated.
Thorium X and products to radiothorium[1].....	3.66	3.60
Thorium C_1 and C_2 to radiothorium[1].....	1.54	1.56
Actinium X and products to radioactinium[2].....	4.67	4.63
Radium emanation and products to radium [3].....	4.11	4.09

[1] McCoy and Viol, loc. cit.
[2] McCoy and Leman, loc. cit.
[3] McCoy and Leman, this paper.

lated by the equation $I = kR^{\frac{3}{2}}$, the correctness of which may be considered as already established, shows that only those members which we

[1] Phys. Zeit., 7, 489 (1906); Le Rad., 3, 170 (1906).
[2] Rutherford, Radioactive Substances, p. 447 (1913).
[3] Boltwood, loc. cit.

have considered play significant parts in the α-ray activity of the radium series, and that the accepted ranges are at least approximately correct.

In Table V the results of the recent investigations carried out in this laboratory along analogous lines are brought together.

The values headed "Found" are the relative observed α-ray activities of the indicated substances. The calculated values were obtained by means of the equation $I = kR^{\frac{2}{3}}$, according to which the number of ions produced by an α-particle is proportional to the $2/3$ power of its range.

KENT CHEMICAL LABORATORY,
UNIVERSITY OF CHICAGO,
March 3, 1915.

THE FLUORESCENCE OF SOME FROZEN SOLUTIONS OF THE URANYL SALTS.

BY H. L. HOWES.

IN the recent work done by Nichols and Merritt[1] on frozen solutions of the uranyl salts at liquid air temperature it was noticed that there were various changes in the spectra of those solutions at temperatures intermediate between + 20° C. and − 185° C. The object of this investigation was to study these spectra at the intermediate temperatures. It was known that in general the spectra consisted of rather broad bands with well marked crests, and that the frequency interval between the bands was constant.

EXPERIMENTAL METHOD.

For the study of the spectra, except where otherwise specified, a Hilger constant deviation spectrometer was used.

The apparatus for the cooling and excitation of the substances under observation was designed to enable the observer to hold the temperature of the specimen constant at any temperature between 0° and − 180° C. The mounting consisted of a cylindrical copper block *M* (Fig. 1), the top of which was bored to receive a small test-tube *F*, which contained the fluorescent solution. The side of the block was channelled to let the exciting light fall on the specimen; and to let the fluorescent light out. To the bottom of this copper block was soldered a cylinder of sheet copper, which could be partially or completely covered by the liquid air in the unsilvered Dewar bulb *D*, thus producing different temperatures in the specimen. This mounting was rigidly suspended from above by partially non-conducting material. The Dewar bulb was fastened to an adjustable support *H*, and the mounting could be submerged in the liquid air to various depths by raising or lowering the bulb by means of cord *R*.

Fluorescence was excited by the rays from a carbon arc *A*. The light passed successively through a water cell *W*; a large short-focused condenser *C*; and a solution of ammonio-copper sulphate *B*. This solution absorbed all of the exciting light of a wave-length greater than .4780 μ, so that the fluorescent light, which entered the collimator slit *S* of the spectrometer, could be viewed on a black background.

[1] PHYS. REV., Vol. III., June, 1914.

A small resistance coil T was inserted in a glass tube, which was always placed in the middle of the solution. The temperatures were recorded on a Callendar recorder. The massive copper block M served to reduce the vertical temperature gradient in the frozen solution to

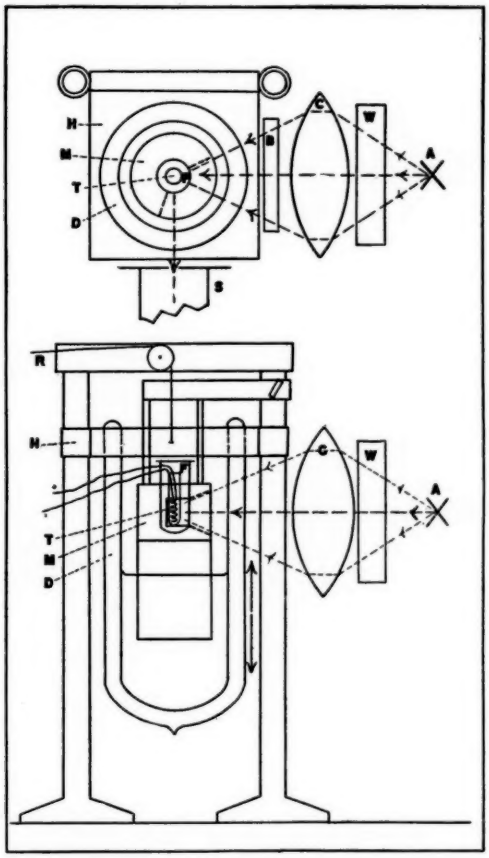

Fig. 1.

less than 1° per centimeter. It made the apparatus rather slow in responding to changes, but afforded an excellent control of temperature.

The salts were carefully weighed and "normal" solutions were prepared.[1] Acid solutions were made by adding a definite volume of the commercial concentrated acid to a definite volume of a water solution of known concentration.

Although readings were taken and tables made in Ångström units

[1] The term "normal" solution, as used in this paper, means one which contains the same number of grams of solute to the liter of solvent as the number which represents the molecular weight of the particular salt dissolved.

of wave-length the diagrams of spectra were plotted on an arbitrary scale of frequencies; *i. e.*, 1/A. u. $\times$ 10^4. Both scales were placed under each plot for the convenience of the reader.

PRELIMINARY STATEMENT OF THE RESULTS.

In general, when a solution of a uranyl salt was cooled slowly to liquid air temperature its spectrum changed in two or more ways. The spectrum always appeared brighter at lower temperatures than at room temperature. There was always a shift of the spectrum, either toward the red or toward the violet, due to the change in temperature.

Generally, too, the bands were narrower at lower temperatures.

The more dilute the solutions the dimmer were the spectra.

In the uranyl nitrate solutions the rate at which the solution was cooled determined what spectrum would be produced, as regarded the number and position of the bands.

The effect of diluting the water solutions with small proportions of acid was to produce a shift in the positions of the bands, and in larger proportions, to entirely change the character and appearance of the spectrum.

URANYL SULPHATE IN WATER.

Uranyl sulphate presented spectra consisting of broad bands. At + 20° the spectrum of the normal solution consisted of four dim bands, which were equally spaced when plotted on a scale of frequencies. The bands shifted toward the violet as the temperature was lowered. This shift attained a maximum when the temperature was approximately − 100°. (See Table I.) On further fall in temperature the bands shifted toward the red. As a result of this reverse shift the bands occupied nearly the same positions at − 180° as they formerly had at a temperature of − 60°.

The one-tenth normal solution of the uranyl sulphate gave a series of bands which occupied nearly the same positions as those of the normal solution. These bands attained their maximum shift toward the violet at − 90° and then shifted towards the red. To ascertain the effect of the rate of cooling a test-tube containing this solution was suddenly plunged into liquid air and excited to fluorescence. The bands were similar to those of the same solution which had been slowly cooled. If there were any change in position it was within the experimental error of observation.

The .01 normal solution showed the shift toward the violet and the reverse shift. The temperature at which maximum shift occurred was − 100°.

The .001 normal solution gave vague broad bands at all temperatures. All of the bands were found to be nearer the violet than those of the stronger solutions. The maximum shift toward the violet was found to occur when the temperature was − 120°.

TABLE I.

Uranyl Sulphate in Water; Normal Solution.

Temperature.	Band *b*.	Band *c*.	Band *d*.	Band *e*.	Band *f*.	Band *g*.
+ 20°	....	....	5,641	5,383	5,143	4,927
0	....	....	5,641	5,383	5,141	4,926
− 35°	....	5,934	5,641	5,378	5,141	4,927
− 60°	6,229	5,928	5,637	5,376	5,137	4,924
− 90°	6,227	5,923	5,635	5,370	5,131	4,919
−120°	6,230	5.923	5,634	5,370	5,133	4,919
−150°	6,235	5,924	5,634	5,373	5,136	4,921
−180°	6,241	5,924	5,636	5,375	5,140	4,926

Jones and Strong,[1] in their study of the absorption spectra of the uranyl salts, noticed that the absorption band at 4,910 A. u. shifted 15 A. u. toward the red when the temperature was raised from + 5° to + 84°. This is in agreement with the movement of fluorescence band *g* (Table I.) normal solution which shifted 8 A.u. toward the red when the temperature was raised from − 90° to + 20°. The shift is the same in direction in both the fluorescence and absorption spectra of the normal solution for temperatures above − 100° C.

URANYL SULPHATE IN SULPHURIC ACID.

The one-tenth normal aqueous solution was added to the sulphuric acid, the first solution containing 40 c.c. of the solution to 1 c.c. of the acid. The spectrum was shifted towards the violet at − 90°. When the cooling process was carried to − 180° the bands shifted back toward the red.

The bands occupied approximately the same position as did the bands of the 1/10 normal aqueous solution at the corresponding temperatures. Band *g* was the exception, as it was shifted, at all temperatures, nearer to the red. This decreased the frequency interval between bands *f* and *g* at all temperatures.

Another acid solution was made by mixing equal volumes of the 1/10 normal solution and of the acid. The spectrum of this solution, at + 20°, was nearer the red than that of the aqueous solution at + 20°.

[1] Carnegie Inst. of Washington, No. 130, p. 109.

Jones and Strong[1] also found that the absorption spectrum of the uranyl sulphate was shifted toward the red by the addition of sulphuric acid to the aqueous solution. The effect of slowly cooling this solution to − 185° was to produce a marked shift toward the violet. Band *g* shifted 72 A.u. between + 20° C. and − 180° C. This shift toward the violet even continued through the range from − 90° to − 180°. The bands were equally spaced in frequency units.

URANYL POTASSIUM SULPHATE IN WATER.

The spectra of the aqueous solutions of this salt resembled those of the single sulphate in appearance. The bands were broad, and, in the stronger solutions, very brilliant.

The 1/15 normal solution was almost saturated at + 20° C. When the temperature was lowered the spectrum showed a slight increase in the frequency interval, and a pronounced shift when − 150° was reached. Between − 120° and − 150° the shift toward the red which began at 0°, increased rapidly, and continued to the lowest temperature. At all temperatures between − 30° and − 185° the space between the bands was approximately 86 units, on the scale of frequencies.

The 1/150 normal solution gave spectra which at first shifted slightly toward the violet and then shifted toward the red. The frequency interval was again 86 units.

To ascertain the effect of sudden cooling on the bands of this solution the solution was suddenly plunged into liquid air. The spectrum at − 180° was the same as that of the slowly cooled solution as regarded position and appearance of the bands.

The 1/1500 normal solution gave vague spectra. The bands appeared to be almost smothered by the continuous fluorescent spectrum which formed the background. Another trial with the same solution gave a spectrum which showed no decided tendency to shift toward the red.

The 1/15,000 normal solution gave a spectrum which consisted of dim, hazy bands. The effect of dilution was to produce an enormous shift of all of the bands toward the violet; and to further decrease the interval between bands. The effect of lowering the temperature was to shift the bands toward the violet until − 120° was reached; while on further cooling a reverse shift toward the red occurred.

The 1/150,000 normal solution gave, at − 185°, a spectrum which consisted of three very dim bands. The middle band, at 5239 A. u. corresponded in position to the band at 5235 A. u. of the 1/15,000 normal solution, but the interval between the bands was smaller.

[1] Loc. cit., p. 135.

The effect of *dilution* on the frequency interval was to decrease it. Both the 1/15 and 1/150 normal solutions had bands which were spaced 86 + frequency units apart; the 1/1,500 bands were 82 units apart; the 1/15,000 bands were 80 units apart, and the 1/150,000 bands 77 frequency units apart.

Uranyl Potassium Sulphate in Sulphuric Acid.

Fig. 2 shows the bands of an acid solution made by adding 5 c.c. of the 4/15 normal solution to 1 c.c. of sulphuric acid. The spectra shifted toward the violet when the solution was cooled, and attained their maximum shift at − 120°. Further cooling to − 180° caused the bands to shift back toward the red. In the manner of shifting, the spectra of this solution resembled closely those of the stronger solutions of uranyl sulphate in water. The frequency interval became shorter as the temperature was lowered, but appeared to be constant at any one temperature.

Another sulphuric acid solution was made by adding 1 c.c. of the 4/15 normal solution to 1 c.c. of the sulphuric acid, which showed a constant tendency to shift toward the violet as the temperature was lowered from + 20° to − 180°. The total shift amounted to about 40 A. u. Here, too, the interval between the bands decreased as the temperature of the solution was lowered.

The last solution studied was the most interesting. It was made by adding one part of the solution to fifty parts of sulphuric acid. It was observed that the shift was quite irregular until a temperature of − 150° was reached, when the bands nearer the violet doubled. At − 180° there was a greater tendency toward resolution. The component bands were evenly spaced on the frequency scale, and formed separate series.

Uranyl Chloride in Water.

The spectra of the uranyl chloride in solution consisted of single bands, which were about 75 A. u. in width and were separated by a black background. In the latter respect they differed from the spectra of the sulphates, as the background for the bands of the sulphates was always filled with a very dim continuous fluorescence. The crystalline chloride was very deliquescent and very soluble in water, but the spectra were not nearly so brilliant as those of the sulphates.

The bands of the saturated solution were first measured at − 90°, and were found, except for the two end bands, to be evenly spaced in frequency units. When the temperature was gradually lowered to − 180° the bands appeared brighter, and shifted slightly towards the red,

so that band 5154 A. u. shifted only six A. u. as the temperature was reduced to − 180°.

The effect of adding more water to make a 3.0 normal solution was to shift the spectrum as a whole about 15 A. u. toward the violet, without changing the actual distances between the bands. The effect on the

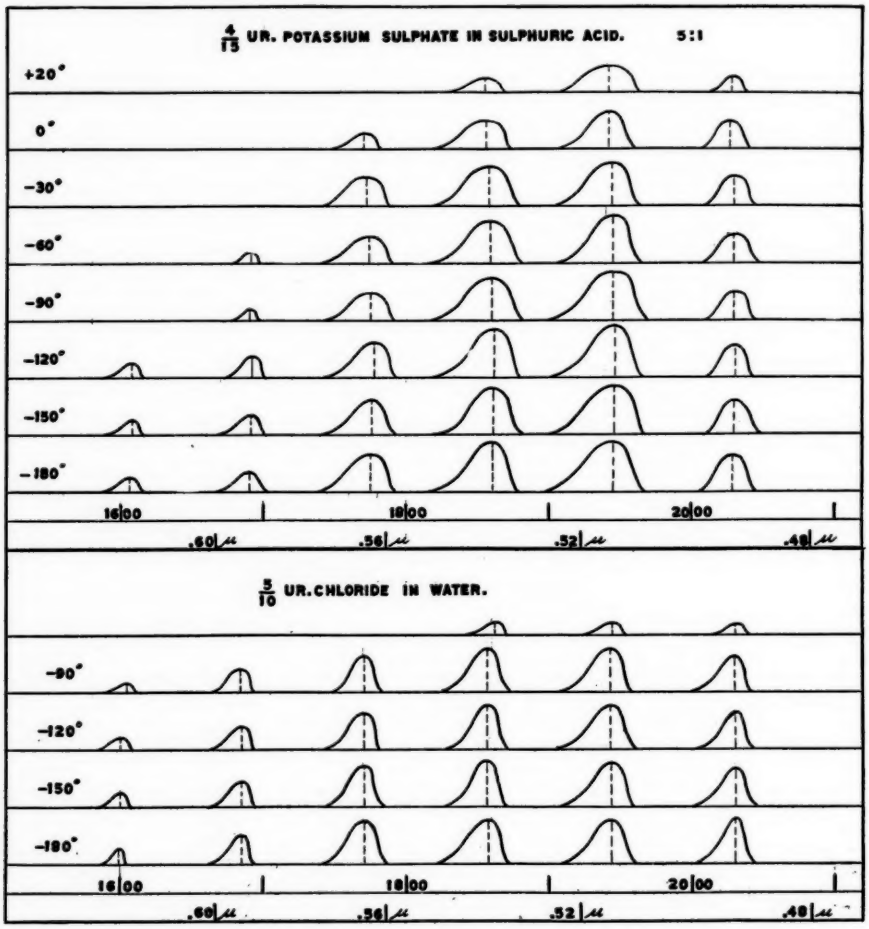

Fig. 2.

positions of bands of changing the temperature was small. The shift was slightly toward the red for all bands except the violet band, which was fixed. This band, as well as the red band, was again closer to its neighboring band than the constant interval of the series.

The 1.5 normal solution was still more stable, since the bands, except for the red, are not moved by changing the temperature. The .5 and .05 normal solutions were also practically unaffected by changes of temperature. See Fig. 2.

Extreme dilution with water would possibly have produced a shift in the spectrum as a whole, but so far as these results go, it would seem that the aqueous solutions of the uranyl chloride are the most stable of any of the uranyl salts in solution.

URANYL NITRATE IN WATER.

The first results obtained by changing the temperature of various solutions of the uranyl nitrate were often contradictory. These results were only made to accord when the same slow method of cooling the solution was employed. Nichols and Merritt[1] found that the spectrum of uranyl nitrate consisted of alternate broad and narrow bands. An

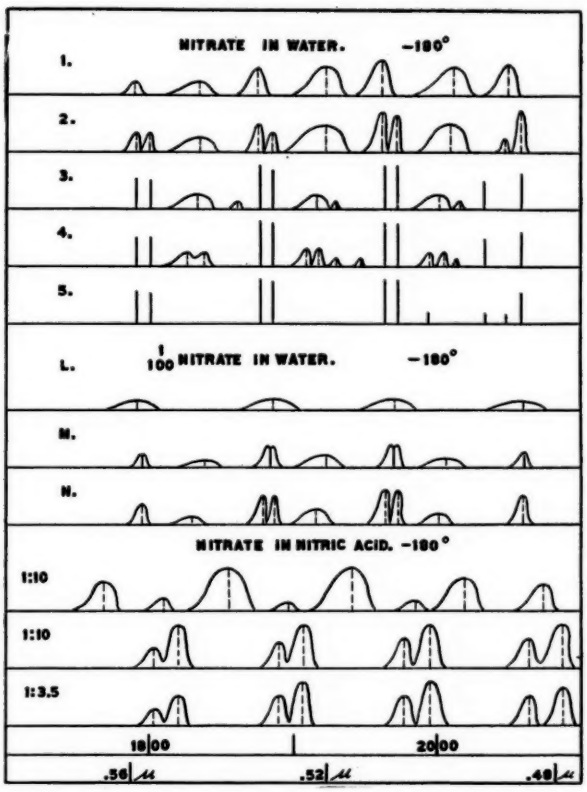

Fig. 3.

entirely different spectrum was obtained from the same salt by a slower method of cooling to liquid air temperature. Five different spectra were photographed from the same solution at − 180°. (See Fig. 3.) These five spectra show the different degrees of resolution obtainable

[1] Loc. cit., p. 459.

by varying the rate of cooling. No. 1 was obtained by suddenly plunging a test-tube of the normal solution into liquid air: numbers 2, 3 and 4 show the varying degree of resolution obtained by slower cooling. No. 5 required about ten minutes to cool from + 20° to − 180° C. The double bands of this spectrum are in the same position as those of the crystallized nitrate at − 180° and all well resolved.

The spectra of the 1/100 normal solution were similarly affected (see Fig. 3) by retarding the rate of cooling. Spectra *L*, *M* and *N* are the results of successively slower rates of cooling.

Uranyl ammonium nitrate and uranyl potassium nitrate gave almost as good resolution as the uranyl nitrate.

THE EFFECT OF TEMPERATURE ON A SLOWLY COOLED NORMAL SOLUTION OF URANYL NITRATE.

Since the changes in the spectrum of the normal solution are very striking and also typical of several other more dilute solutions a detailed study of them was made. (See Fig. 4.) At + 20° only two dim bands were seen, one at 5,323 A. u. and the other 5,088 A. u. At 0° a slight increase in intensity was noted, so that four bands could be measured, and at − 25° several phenomena occurred simultaneously. The Callendar recorder indicated a very sudden *rise* in temperature to − 18°, while the background, which previously had been very dim, became brighter. A portion of the background came up so strong as to unite with and broaden each band on the violet side, thereby producing very broad flat bands of double the width of the original bands. This occurred after the phenomenon of under cooling. At the same time there was a five-fold increase in the intensity of the bands.

At − 46° the half of each band nearest the violet began to decrease in intensity while the other half grew brighter, which caused a marked decrease in the width of the bands. It was found by reversing the cooling process that the − 60° spectrum persisted while the temperature was raised to the cryohydrate point at − 18°, when it suddenly faded into the original dim spectrum. There was no suggestion of the broad flat bands at − 40° which were produced on cooling.

With the aid of the spectrophotometer it was again found that a marked increase in brightness had occurred; for the crests of the bands were 85 times as bright at − 60° as at + 20°. It will be noted, by referring to Fig. 4, that the bands doubled at − 90°, and that a dim intermediate series of bands appeared. Subsequent cooling increased the resolution of the doublets without shifting them very much, and also produced a few new bands. At − 180° the doublets were 85 + fre-

quency units apart and formed two series; the unresolved red band being a member of one series and the blue band at 4,855 A. u. a member of the other. The very dim intermediate bands formed two different series, one of 85 and the other of 84 frequency units.

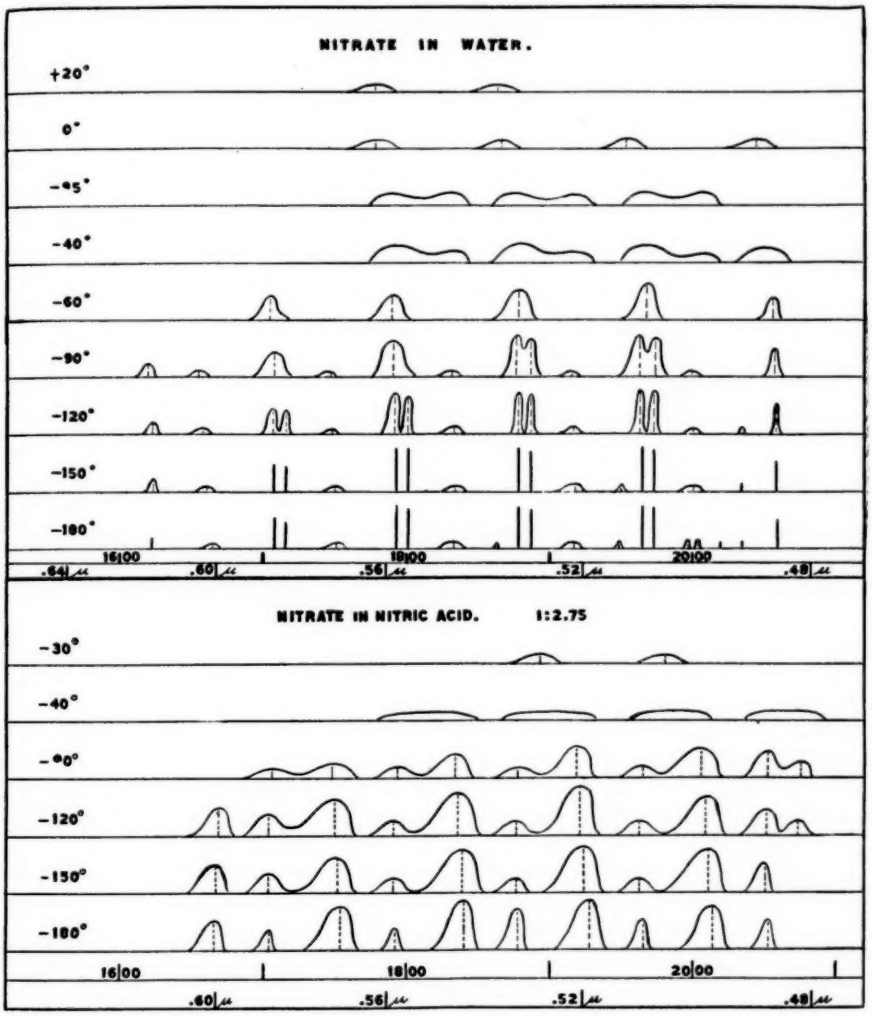

Fig. 4.

The 1/10 normal solution gave similar spectra when the temperature was lowered, but the resolution was not so complete.

The effect of further dilution with water can be seen in Fig. 5. The 1/1,000 normal solution shows single broad bands, considerably shifted with respect to the intermediate bands of the more concentrated solutions.

The 1/10,000 bands are in nearly the same positions as were the doublets of the normal solution.

URANYL NITRATE IN NITRIC ACID.

The normal aqueous solution was almost unaffected by small amounts of nitric acid, as a study of Fig. 6 will show. The spectrum at the top, marked 20 : 1, was produced by exciting to fluorescence a solution of 20 c.c. of the normal solution to 1 c.c. of acid, after it had been slowly cooled to liquid air temperature. The acid brings out more of the very dim bands, and tends to decrease the resolution of the strong doublets. There was no shift, or marked change in resolution until the spectrum

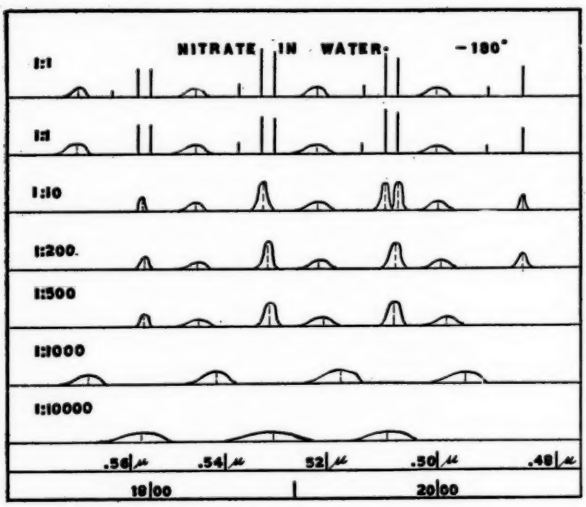

Fig. 5.

of the 1 c.c. of solution to 2.5 c.c. of acid mixture was observed. In the next spectrum, 1 : 2.75, a striking increase in intensity of the broad dim bands was noticed, while the doublets were replaced by single bands. The spectra of these two solutions at higher temperatures are shown in Figs. 4 and 6.

The spectrum following, that of a solution of one part normal, aqueous, to five parts nitric acid, was of the same type as the 1 to 2.75 solution, but shifted twelve frequency units toward the violet. The *same spectrum persisted in the four dilute solutions which follow, even when there was only one part of the aqueous solution to one thousand parts of concentrated nitric acid.*

The effect of nitric acid on the spectra of more dilute aqueous solutions of the nitrate was to produce broad banded spectra similar to those we

have just studied. Often unstable solutions resulted, so that it was found difficult to reproduce the spectra of such solutions. Nor was this phenomenon of obtaining two or more distinctly different spectra con-

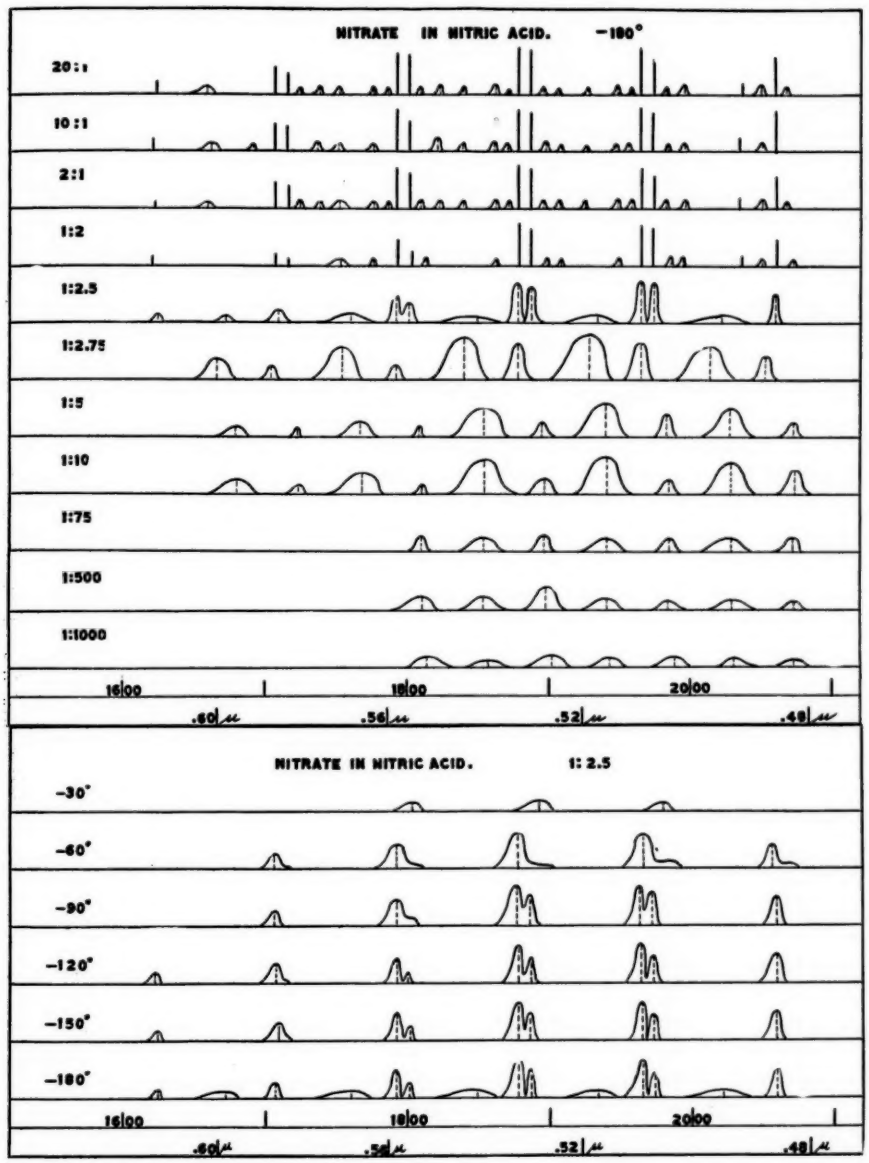

Fig. 6.

fined to the dilute aqueous solutions with nitric acid. The three spectra, at − 180°, shown at the bottom of Fig. 3 illustrate this point. The

first two spectra, although entirely different, were produced from a solution of one part normal aqueous solution with ten parts nitric acid. The first spectrum was obtained after very slow cooling, the second, after a rather slow cooling, to liquid air temperature, but this second spectrum is identically the same as that obtained from a solution of one part normal to three and one half parts nitric acid when the usual slow cooling was employed. It was found that the 1 : 10 solution might give either

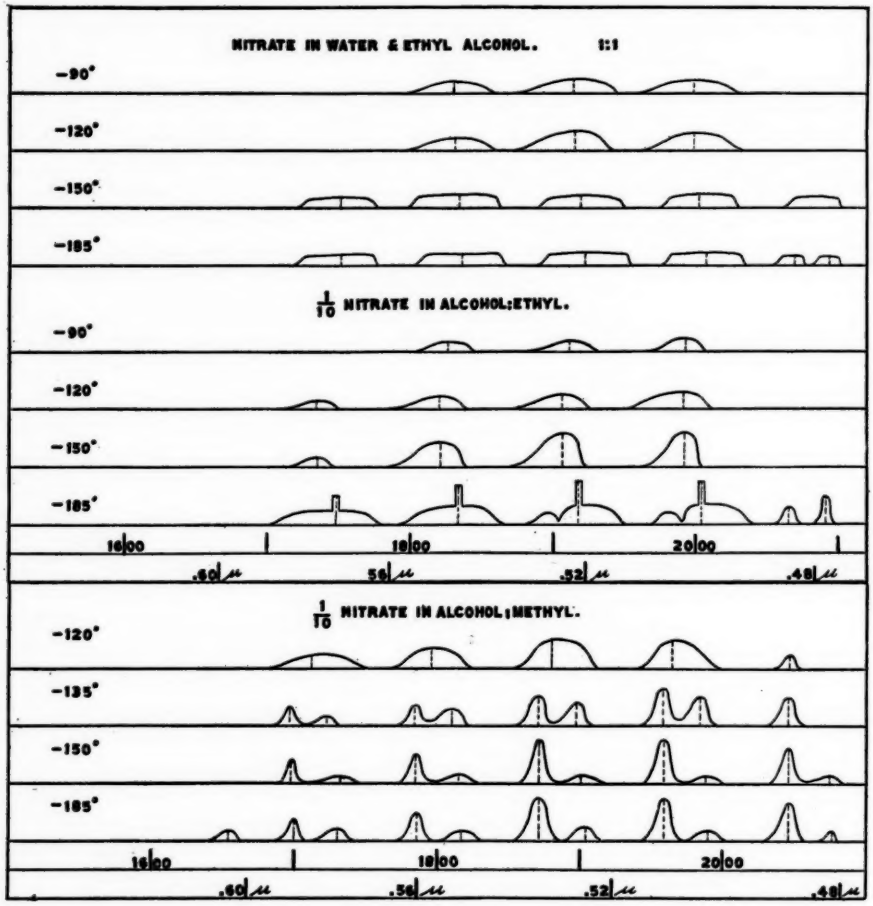

Fig. 7.

spectrum under apparently the same conditions of cooling, in fact, it was somewhat accidental as to which spectrum would appear.

URANYL NITRATE IN ALCOHOL.

The fluorescence of an alcoholic and an aqueous normal nitrate solution, equal parts, showed an entire change in appearance from the

spectrum of the aqueous solution. (See Fig. 7.) These bands occupied approximately the same positions as the intermediate bands of the normal nitrate in water at − 180°; but were broader and much less intense. The strong doublet series of the aqueous solution appeared to be entirely quenched by the alcohol. The frequency interval is the same for this solution as for the aqueous solution.

Another alcoholic solution was made by dissolving uranyl nitrate crystals directly in ethyl alcohol. (See Fig. 7.) The bands shifted toward the red at − 120°, and drifted toward the violet until − 150° was reached, when they began to shift back rapidly toward the violet while the crests protruded in a striking manner. It is important to note that these sharp crests are in the same positions at − 185° as the bands of the nitrate in water and ethyl alcohol.

A solution of the uranyl nitrate in methyl alcohol (see Fig. 7) gave series which both in manner of doubling and appearance closely resembled the aqueous solutions. The stronger members of the doublets are nearly

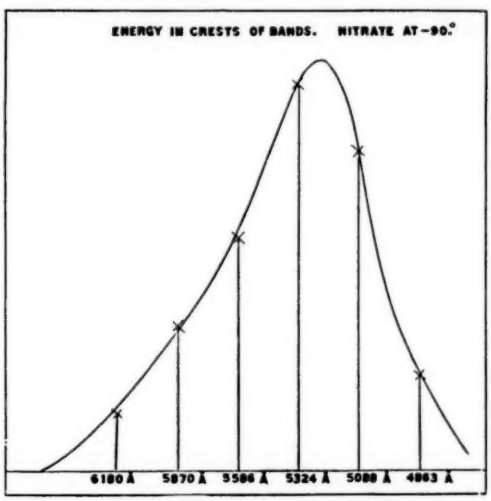

Fig. 8.

in the same positions as the narrower members of the doublets of the quickly frozen aqueous solution (see Fig. 3), but the dim broad bands are shifted very decidedly toward the red in comparison with the positions of the broad bands of the aqueous solution. The doublets of the methyl alcohol solution also formed two series of bands with a constant frequency interval.

DISTRIBUTION OF ENERGY IN THE BANDS OF URANYL NITRATE.

By the aid of a Hilger spectrophotometer, the brightness of the crests of the bands was compared with the brightness of the acetylene flame

spectrum. These values were multiplied by the ordinates of the corresponding wave-lengths of the energy curve for acetylene.[1] (See Fig. 8.) Nichols and Merritt[2] found such a curve for the distribution of energy in the bands of several of the uranyl salts at room temperature, as well as for the distribution of energy throughout the spectra.

SUMMARY AND CONCLUSIONS.

The changes produced in the spectra of the aqueous solutions of the uranyl salts by slowly lowering the temperature from room temperature to liquid air temperature are:

1. A proportionate increase in the intensity of all of the bands.
2. A shift either toward the red or the violet.
3. A narrowing of the bands and in some solutions a tendency towards resolution.
4. A slight change in the frequency interval between bands, although it appears to be constant at any given temperature. The only exception to this statement is the fact that occasionally an extreme red or blue band does not join the constant interval series.

A suddenly cooled solution of the uranyl nitrate has a different spectrum from the same solution when slowly cooled. This is also true of the double nitrates.

Dilution with acid produces larger shifts than dilution with water and often radically changes the appearance of the bands.

The alcoholic solutions are invariably dim and broad-banded, and offer a less interesting field for investigation than the aqueous solutions.

The fact that two or more different spectra can be obtained from the same solution of the nitrate may be explained by assuming that when a radically different spectrum is produced a different hydrate is formed.

The extraordinary shifts and other changes in the spectra recorded are most readily explained by assuming, as has been done in the case of a study of the fluorescence and absorption spectra of the uranyl salts recently completed by Professors Nichols and Merritt and to be published shortly in the PHYSICAL REVIEW, that the bands in such spectra are complex, and consist of overlapping components, which vary relatively in intensity with changes in temperature.

Many thanks are due to Professors Nichols and Merritt and other members of the staff for the interest that they have taken in this work.

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[1] Coblentz, Bur. of Standards, Vol. 7, No. 2, p. 259.

[2] PHYSICAL REVIEW, Vol. XXXII., p. 358.

CHARGED SURFACE LAYERS FORMED ON THE ELECTRODES OF VACUUM TUBES.

By K. T. Compton and L. W. Ross.

Introduction.

SEVERAL years ago one of the writers observed that metals which had been used as cathodes in an X-ray discharge, in the attempt to obtain fresh clean surfaces, exhibited abnormal and very erratic photoelectric properties. In some cases the emitted electrons appeared to possess extremely high velocities while in other cases a strong field in addition to the action of the light was required to free the electrons from the surface. A later investigation[1] showed that such apparently abnormal photoelectric velocities, which had been observed by several investigators, were due to some sort of surface phenomenon which had the effect of greatly changing the contact difference of potential between the emitting and receiving electrodes and thus exposing the electrons to a strong accelerating or retarding field. Recently Seeliger[2] has found evidences of an electrical double layer, formed on the cathode of an X-ray bulb, which has the effect of changing the normal potential of the cathode by about 3 volts.

Because of the frequent use in research of metallic films sputtered from cathodes and of metals which have been exposed to X-ray discharges it is of practical importance as well as theoretical interest to understand the nature of this surface phenomenon, the cause of its erratic behavior and the methods by which it may be controlled.

For the experimental investigation we employed the following apparatus. Enclosed in the brass cylindrical vessel MN were the disk-shaped plates P and B, of platinum and brass respectively, which served as the electrodes for the vacuum discharge. The vessel could be opened at FF, where the upper part fitted into an accurately ground groove cut in the base and around which wax was melted to render the joint airtight. The vacuum was maintained by a Gaede pump connected to the vessel by the brass tube A.

The effect of X-ray discharges on the nature of the surfaces of the

[1] Otto Stuhlmann and Karl T. Compton, Phys. Rev., Vol. 2, p. 199 (1913).

[2] Phys. Zeit., XIV., p. 1273 (1913).

plates P and B was determined by measurements of the contact difference of potential between the opposing surfaces of these plates. These measurements were made by Kelvin's method.[3] The plate P could be moved up or down by turning the ground-glass joint J_1 and this formed, with B, a parallel plate condenser of variable capacity. The plate B was connected with a quadrant electrometer E. When the potential of the plate P was adjusted by the potentiometer S so that no deflection of the electrometer was observed when the plate P was raised or lowered, then the voltmeter V indicated the contact difference of potential between P and B.

The plate B was so large (6 cm. diameter) as to leave only one milli-

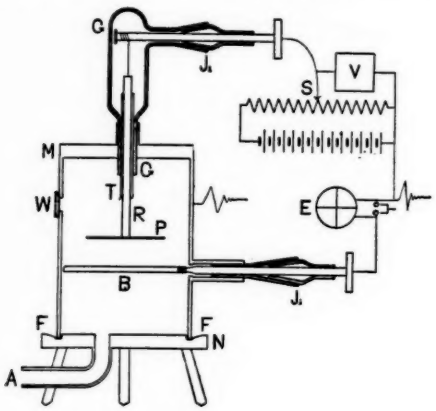

Fig. 1.

meter clearance between it and the vessel MN. During each X-ray discharge the plate B and the vessel MN were earthed and the plate used as anode or cathode as desired. In this way the lower side of the plate B was shielded from the effects of the discharge. By rotating the ground-glass joint J_2 the plate could be reversed and its shielded face tested for contact potential.

The sensitiveness of the system was such that one volt difference of potential between B and P caused a deflection of about 40 millimeters when the plate P was raised or lowered. In most of the work quickness rather than high accuracy was desirable.

Experiments with Clean Surfaces.

For the first tests the inside of the vessel was rendered as free as possible from wax and insulating materials. The inside of the vessel and all metal parts were vigorously polished with emery and tripoli

[3] Lord Kelvin, Phil. Mag., Vol. 56, p. 82 (1898).

powders and wiped clean. All insulation on the inside of the vessel was shielded from the direct discharge and so disposed as to reduce to a minimum effects due to charges accumulated on the insulation.

Under these conditions we passed discharges of various durations

TABLE I.

Duration of Discharge.	Contact Potential.	Duration of Discharge.	Contact Potential.
0 sec.	0.30 volt	80 sec.	−0.25 volt
2	0.21	140	0.00
12	−0.04	440	0.15
20	−0.23	1,040	0.12
40	−0.25	1,940	0.06

between the plates P and B, using P as the cathode, and measured the contact difference of potential after each discharge. Some typical results are indicated in Table I. The contact difference of potential is called positive when of the normal sign, *i. e.*, brass positive with respect to platinum. Evidently the discharge produces a very slight disturbance in the contact difference of potential. A comparison of these results with others in which less care was taken to eliminate wax from the vessel indicates that these are due to slight traces of wax (possibly due to the vapor pressure of the wax in the joints) remaining in the vessel in spite of the efforts made to avoid them.

EXPERIMENTS WITH INSULATING FILMS.

The effect is on the wax film. When films of various kinds of wax were placed on the plate P and this plate was used as anode or cathode, the apparent values of the contact difference of potential after the discharges varied between $\pm$ 500 volts and the value in every case was unchanged by reversing the plate B and testing with its shielded side opposed to P. But when the plate P was cleaned and wax was placed on the upper side of the plate B it was found, after each discharge, that the high contact difference of potential between B and P entirely vanished when the clean side of B was placed opposite P. These tests show conclusively that the abnormal contact potentials are due to and exist in the insulating films.

The effect of reversing the plate was as here described only provided the discharge had not been excessively heavy and long. It was found that very heavy discharges vaporized the wax, which condensed all over the inside of the apparatus and vitiated the above tests.

The nature of the effect depends on the conditions of the discharge. We

found that the nature of the effect did not depend appreciably on the degree of vacuum, within wide limits, but that it was determined jointly by the time and the intensity of the discharge. Typical sets of measurements are shown in Table II. The effect on the wax film of a short discharge or of a weak one is to leave the outer surface of the film coated with an electrified layer of sign opposite to that of the waxed plate during the discharge. A long and heavy discharge reduces the intensity of electrification of the layer and may even reverse the sign.

TABLE II.

Discharge.		Contact Potential. Soft Wax on		
Time.	Nature.	Pt. Cathode, Volts.	Pt. Anode, Volts.	Brass Anode, Volts.
Before.....	Sputtering	0.40	0.40	0.40
0.5 sec.....	Weak	−120	35	− 75
Several 0.5 sec.....	Medium	−160	130	−130
30 sec.....	Heavy	− 50	− 6.5	− 60
30 sec.....	Heavy	− 30	.....	− 40
1 min.....	Heavy	− 10	−13	− 12
1 min.....	Light	−100	2	
1 min.	Heavy	− 45	− 6.5	
Several 0.5 sec.....	Heavy	−160	75	−100
15 min.....	Heavy	2	−11	− 2

These contact potentials decay with time. A typical rate of decay curve is shown in Fig. 2, in which the waxed plate P was the anode. This

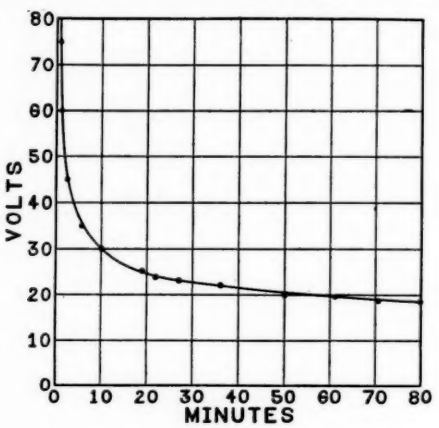

Fig. 2.

change is initially much too rapid to be represented by a logarithmic curve. The largest values in Table II. are evidently not the maximum values since the measurements could not be made instantaneously

after shutting off the X-ray discharge. The rate of decay was distinctly more rapid in air than if a good vacuum was maintained.

DISCUSSION OF THE RESULTS.

These results are consistently and reasonably interpreted as due to two processes which are effective during the discharge. The first of these is the deposition of a layer of gaseous ions over the outer surface of the insulating film and the second is a convection current in the wax itself, whereby charged portions of the viscous wax are repelled from the metal to the outer surface. Obviously these two processes tend to give rise to contact potentials of opposite sign and the one which predominates depends on the nature of the discharge. We should expect the latter effect to be relatively important when the wax is heated and thus rendered less viscous. This was actually the case, for in Table II. we noticed that long and heavy discharges, which warmed the wax, produced effects of the latter sort. Short, light discharges on the contrary, produced strongly charged layers of sign opposite to that of the plate during the discharge.

In this connection it is significant that the largest effects due to convection currents in the wax occurred when the wax was on the anode, subject to the intense heat developed by the bombarding cathode rays. In this position only was the sign of the resultant potential easily reversed by long heavy discharges. It is also significant that long heavy discharges produced relatively larger effects when the wax was on the platinum plate than when it was on the brass plate, for the platinum plate was thin and of comparatively small heat capacity and its temperature was more easily raised by the discharge. In every case in which the reverse effect was marked evidences that the wax had been strongly agitated during the discharge were noticed when the apparatus was taken apart. This roughening of the surface was not noticed after short or light discharges.

This explanation of the phenomena is strongly supported by experiments in which sealing wax and stopcock grease were substituted for the soft wax on the electrodes. We should expect, in the case of sealing wax, that the effect due to the deposited ions would strongly predominate and that, because of the high viscosity, the maximum contact potential would be larger and the rate of decay smaller than in the case of soft wax. In the case of stopcock grease we should expect the contrary peculiarities.

We found, with sealing wax, contact potentials larger than 500 volts in the direction to be accounted for by deposited ions. The rate of

decay was very slow. Only once, after a very heavy discharge, did we find a reversal of sign in the contact potential. In this case the wax had been melted by the discharge. With stopcock grease the highest measurement recorded was 21 volts and most values were about 5 volts. We also found that reverse effects, *i. e.*, contact potentials of the same sign as the applied potential, were observed even after applying potentials too small to produce a vacuum discharge, for instance 150 volts. In all cases the rate of decay was very rapid.

CONCLUSIONS.

1. The abnormal contact potentials produced on the electrodes by high potential discharges are due to and exist in insulating films such as wax or grease on the surfaces of the electrodes and are reduced or eliminated by shielding or avoiding all such substances.

2. On insulating films of small viscosity surface charges are produced by convection currents in the film set up by the applied field, even though this field may be too small to produce a vacuum discharge.

3. During a vacuum discharge a charged layer of gaseous ions is deposited on the surface of the insulating film. This charge is of a sign opposite to that of the potential of the electrode during the discharge and is therefore opposite to that produced by convection currents.

4. The apparent contact difference of potential is the resultant of these two effects, whose relative importance depends on the viscosity of the film and the nature of the discharge.

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AN ATTEMPT TO DETECT A CHANGE IN THE HEAT CONDUCTIVITY OF A SELENIUM CRYSTAL WITH A CHANGE IN ILLUMINATION.

BY L. P. SIEG.

Introduction.—The fact that selenium changes its electrical conductivity so markedly with illumination has no doubt led many investigators to consider the possibility of a change in its heat conductivity with a change in the illumination. This has been of especial interest since the development of the electron theories for both kinds of conduction. However, careful search has revealed but one paper; that by Bellati and Lussana[1] bearing directly on the subject. These authors worked with a thin disc of crystallized light-sensitive selenium. The disc was painted with a thin coat of the red double iodide, Cu_2I_2, HgI_2. This substance turns chocolate brown at about 70° C. and so the color serves as an indicator of the extent on the disc where the above temperature has been attained. They heated a point of the disc with an electrically heated platinum wire. In the sunlight the increase in the thermal conductivity over that in the dark amounted, in one case cited, to about ten per cent. They noted further that the percentage change in the thermal conductivity agreed well with the percentage change in the electrical conductivity where exposure was made to the same light.

Some experiments of my own, performed on a selenium crystal are in serious disagreement with the above conclusions, and are here presented.

Theory of the Experiment.—It seems very questionable whether any simple electron theory is capable of explaining the light electric actions in selenium. Even assuming constant illumination one should be slow to adopt any of the standard electron formulas for heat and electric conduction. Lorentz,[2] Drude,[3] Livens,[4] Thompson,[5] Wilson,[6] and others have developed electron formulas for thermal and electrical conduction in metals. It will not be necessary to repeat these formulas here. It is

[1] Atti del R. Inst. Ven. (6), 5, 19, 1887. Abs. Beib. d. Ann., 11, 818, 1887.
[2] Theory of Electrons, pp. 67, 266.
[3] Ann. d. Phys., 1, 566, 1900; 3, 369, 1900.
[4] Phil. Mag., 29, pp. 173, 425, 1915.
[5] Phil. Mag., 14, 217, 1907.
[6] Phil. Mag., 20, 835, 1910.

to be noted, however, that although these formulas differ in the constants involved, they agree in the essential matter that the ratio of the electrical to the thermal conductivity is a function of the temperature, and is independent of the number of free electrons, their velocities, or their mean free paths. The classic experiments of Jaeger and Disselhorst[1] have given ample experimental verification of this independence. One might expect then that any agency that increases the electrical conduction of selenium, might be expected to increase in a measure the thermal conduction. To be sure we should not expect to find as large an increase for the thermal conductivity as for the electrical conductivity, for selenium is at best a very poor conductor of electricity, and so doubtless a large share of the heat conduction is by means of atoms and molecules, just as is true in the case of electric insulators. Nevertheless, if under the action of light there are more electrons *actually made free*, or if those free have a *greater mean velocity* or *path*, there should be at least a small increase in the thermal conductivity. The experimental results described below show, however, that if there is any such improvement in the heat conductivity it is smaller than the error of these measurements.

Apparatus and Method of Observation.—A modified form of the apparatus described many years ago by Christiansen[2] was used. A form of apparatus was required that would meet several conditions. It was decided to work with an isolated crystal of selenium.[3] It was necessary that the apparatus serve to obtain the heat conductivity and the electrical conductivity both in the dark and in the light, and further if possible that it should serve to get the variation of the above quantities with the temperature. A reference to the figure will make the following description clear. At the base is a brass cylinder through which passes a stream of cold water. This cylinder is about 50 mm. in diameter by 20 mm. high. On top of this are placed in succession the following layers. Outside, and in the form of washers we have, a copper plate, a glass plate, a copper plate, a glass plate, and a copper plate. Inside, and in the form of small discs we have the following five layers: a copper disc, a glass disc, a copper disc, a selenium crystal, and a copper disc. The total height of all five discs is 4.5 mm. The other necessary dimensions are indicated on the figure. The purpose of the outside washers was to form a guard ring having about the same temperature gradient as is to

[1] Preuss. Akad. Wiss. Ber. Sitzungsber., 38, 719, 1899, also Phys. Tech. Reich., Wiss. Abh. 3, 269, 1900.

[2] W. Ann., 14, 23, 1881.

[3] The crystal was kindly given to me by my friend Dr. F. C. Brown. The crystal was a close grown fern-like one made up of small, and very probably, hexagonal spines. For further description see PHYS. REV., Ser. 2, 4, 85, 1914.

be found in the central pile of discs. The various washers and discs were joined together with thin films of glycerin in order to improve the heat conductivity of the junctions. Above the whole is an electric heater. In practice this was separated from the top copper disc and washer by thin cover glass for purposes of electric insulation. Thermo-couples end in the central copper discs, the wires passing through the outer washers as shown, and insulated from them. The solid lines indicate copper wires and the dot and dash lines constantan wires. The

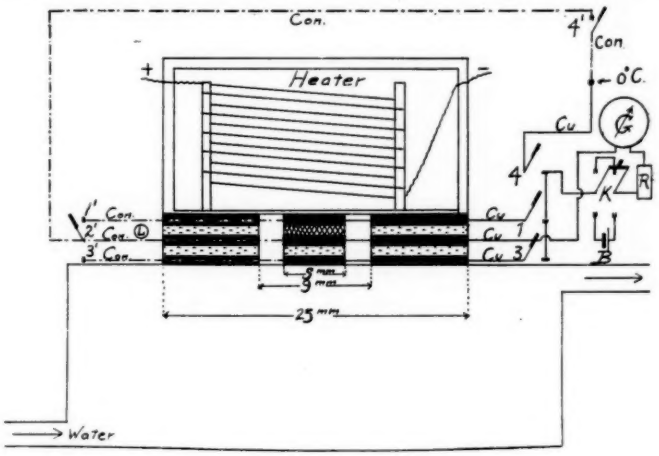

Fig. 1.

switches and other apparatus at the right clearly indicate the manipulations. When the key K is closed upward, the various thermo-couples can be thrown in series with the galvanometer so as to enable one to read the temperature difference between the middle junction No. 2 and any of the others, Nos. 1 or 3, or an outside couple, No. 4, the latter for purposes of calibration. For example if, with K closed upward, key No. 1 is closed and double throw key No. 2′ is connected with terminal, 1′, we have the thermo-couple copper-constantan in series with the galvanometer and the resistances R with the hot (usually) junction in the top copper disc, and the cooler junction in the middle disc. There is an electrical by pass in this circuit, viz., the conduction through the selenium crystal between discs No. 1 and 2, but considering that the whole resistance of the thermo-couple circuit, including the galvanometer, was only about 40 ohms and that the resistance of the crystal was over 1,000,000 ohms we see that no measurable error could enter. If all the keys are opened but No. 1, and K is closed downward, then a cell B is placed in circuit and the electrical conductivity of the crystal can be obtained by the galvanometer deflection. A 25-watt tungsten lamp placed at L could be thrown on or off at will. The light passed through

the clear glass of the upper washer, thus removing much of the heat energy, and so illuminated the selenium crystal. The illumination was sufficient to increase the equilibrium electrical conductivity at ordinary room temperature to nearly three times the dark conductivity.

The theory of the experiments rests on the assumption that the heat that enters the top copper disc passes on down through the pile of discs without loss and is ultimately delivered to the cooling water. In the original method Christiansen used three flat discs with imbedded thermometers and attempted to keep the middle copper disc at room temperature. In this improved guard ring method, if there is about the same temperature gradient between heater and cooler through the discs and the inside of the washers, then there should be no lateral gain or loss of heat so far as the central discs are concerned. If the temperature of the top copper disc is taken as T_1, of the middle one T_2 and of the bottom one T_3, if the thickness of the selenium crystal is d_1 and of the glass disc is d_2, if their thermal conductivities are represented by K_1 and K_2 respectively, and lastly if we assume that the quantity of heat H that enters the top disc likewise leaves the lowest one,

$$H = K_1 \frac{(T_1 - T_2)A \cdot t}{d_1} = K_2 \frac{(T_2 - T_3)A \cdot t}{d_2}.$$

Since the time of flow, t and the areas of the discs, A are the same, we get

$$\frac{K_1}{K_2} = \frac{T_2 - T_3}{T_1 - T_2} \cdot \frac{d_1}{d_2},$$

or with constant thickness of the two discs,

$$\frac{K_1}{K_2} = C \frac{T_2 - T_3}{T_1 - T_2},$$

where C is a constant.

We are thus able to obtain, not the absolute thermal conductivity of the selenium crystal, but rather its ratio to that of glass. For absolute measurements a correction would have to be made on account of the fact that we assume the temperatures of the copper plates to represent the true temperatures of the two sides of the crystal and of the glass respectively. Christiansen gives the necessary correction formulas.[1] In the present investigation no attempt has been made to obtain the absolute thermal conductivity of the selenium crystal. This is because the other question was of paramount interest, and because, on account of the small interstices of the crystal, one would have had to make careful corrections for the heat transmitted by radiation. However, the apparatus is extremely sensitive and reliable for these comparison measurements.

[1] Loc. cit.

The procedure was as follows: The tap water had been running for some hours until it had reached a steady temperature. The heater was left at room temperature in a room, the temperature of which held within a degree during any one set of experiments. After equilibrium had been attained, usually in ten to twenty minutes, the galvanometer readings for $T_1 - T_2$, $T_3 - T_2$, and $T_4 - T_2$ were obtained. T_4 was the temperature of the extra junction and was used for calibrating the

T_1-T_2	T_3-T_2	T_4-T_2	T_1	T_2	T_3	$T_1+T_2/2$	C	k_1/k_2 × Const.	R	State of Selenium.
10.9	− 3.3	6.7	27.2	16.3	13.0	21.8	27	.34	2.48	dark
10.9	− 3.4	6.3	27.6	16.7	13.3	22.1	67	.35	.....	light
12.5	− 4.1	3.7	31.8	19.3	15.2	25.6	33	.37	2.12	dark
12.8	− 4.2	3.7	32.1	19.3	15.1	25.7	70	.37	.....	light
19.4	− 7.1	− 2.3	44.7	25.3	18.2	35.0	41	.39	1.75	dark
19.5	− 7.2	− 2.6	45.1	25.6	18.4	35.4	72	.39	.....	light
27.9	− 9.8	− 7.7	58.6	30.7	20.9	44.7	45	.36	1.67	dark
28.2	−10.4	− 7.7	58.9	30.7	20.3	44.8	75	.38	.....	light
46.1	−17.5	−19.8	88.9	42.8	25.3	65.9	53	.39	1.55	dark
46.4	−17.5	−19.2	88.6	42.2	24.7	65.4	82	.38	.....	light
61.7	−23.8	−28.8	113.5	51.8	28.0	82.7	92	.39	1.28	light
61.7	−24.4	−29.4	114.1	52.4	28.0	82.3	72	.40	.....	dark
73.8	−29.1	−37.4	134.2	60.4	31.3	97.3	72	.40	.....	dark

couples so that galvanometer readings could be reduced to degrees Centigrade. All these readings were taken in a dimly lighted room. The electrical conductivity of the selenium was then obtained by closing key No. 1 and key K downward. The lamp L was now lighted, and after about twenty minutes similar readings were again made. While these readings were being reduced a small current was turned on through the heater. After equilibrium the process was repeated, and so on with various temperature gradients. Typical results of such a set of experiments are found in the table. The galvanometer deflections are for brevity not included. The first six columns are self-explanatory. The seventh represents roughly the mean temperature of the selenium. The column headed C gives the galvanometer deflections and hence a measure of the electrical conductivity of the selenium. The column headed $k_1/k_2 \times$ constant, gives a measure of the relative conductivity of the selenium as compared with the glass. The latter has an unknown, but undoubtedly small temperature coefficient. R is the ratio of the electrical conductivity of the selenium in the light to that in the dark. The last column is self-explanatory. Further examination of the table will make it clear that the ratio k_1/k_2 is not modified by changing from the light to the dark for any given temperature. This means of course, if we assume the light to have no appreciable effect on the thermal

conductivity of the glass, that it has no appreciable effect on the thermal conductivity of the selenium. There seems to be a slight increase in the ratio of k_1/k_2 wtih higher temperatures, but whether this is due to a decrease of the conductivity of the glass used, or an increase in the conductivity of the selenium, or both is impossible to state. If one had at his command a glass, the temperature coefficients of which were known, then he could settle this point.[1]

Incidentally, although the investigation was not directed toward this point, one notes that the electrical conductivity of the selenium both in the dark and in the light increases with increased temperature, but that the ratio of the two decreases. In other words, the selenium while becoming a better conductor of electricity is becoming less light sensitive.

Conclusion.—There may be advanced perhaps a number of reasons why the thermal conductivity was not appreciably changed by the illumination. One might suppose that the number of free electrons is so very small (judging from rough estimates of specific conductivity, about 10^{-12} the number present in copper) that even if there were a threefold increase in their number by the action of the light, that still the number is too small to make an appreciable effect in the thermal conductivity. In other words, the heat conduction in a selenium crystal is largely a matter of the vibrating atoms and molecules.

Another possibility is to assume that the number of free electrons present is not solely determined by the state of light or dark, but is more largely determined by the electric field intensity. If this were so, then one could easily see how the electrical conductivity could be increased without a corresponding increase in the thermal conductivity. The electrons could be assumed to be in an unstable state within the atom, and under the action of the light the instability is increased, but still the electrons are not expelled until an electromotive force is applied. The fact that the resistance of these crystals, and also of selenium cells in general is lowered by increased potential is evidence along this line. The lowered resistance can be interpreted as representing more actually freed electrons.

Whatever the explanation, the experimental results developed that whilst the given source of light increased the electrical conductivity nearly 300 per cent., the same light did not increase the thermal conductivity in any appreciable manner. Considering all possible sources of error, it must certainly have been under five per cent.

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[1] The glass used was supplied by Bausch and Lomb from their regular cover-glass stock.

THE PRINCIPLE OF SIMILITUDE AND THE PRINCIPLE OF DIMENSIONAL HOMOGENEITY.

BY RICHARD C. TOLMAN.

THE writer has recently presented[1] a new postulate, called the principle of similitude, which serves as a successful starting point for the deduction of a considerable number of physical laws. There is a certain similarity between the methods of applying this new principle to the deduction of physical laws and the methods of applying the well-known principle of dimensional homogeneity, and the purpose of the present article is to show, in the first place, *that the essential content of the two principles is in reality quite distinct*, and in the second place that it is *possible to derive important relations from the principle of similitude which cannot be derived from the principle of dimensional homogeneity and vice versa*.[2]

Statement of the Principle of Dimensional Homogeneity.—Let us first state the principle of dimensional homogeneity in such a form that we may later compare its essential content with the content of the principle of similitude.

All of the equations of mathematical physics can obviously be put in the general form

$$A' + B' + C' + \cdots + N' = 0, \qquad (1)$$

where each of the letters A', B', C', etc., expresses some function of the magnitude of a property or a functional combination of the magnitudes of several properties. The principle of dimensional homogeneity requires that all the terms A', B', C', etc., shall have the same dimensions, in other words, that the equation itself shall be unaltered if we multiply every value of length in the equation by some arbitrary multiplier x, every time interval by another arbitrary multiplier y, every mass by z,

[1] PHYS. REV., *3*, 244, 1914; ibid., *4*, 145, 1914.

[2] The writer has intended for some time to point out the exact relation and difference between the theory of similitude and the ordinary theory of dimensions. A more immediate necessity for the present paper, however, is to be found in an article by Dr. E. C. Buckingham on the use of dimensional reasoning. (PHYS. REV., IV., 345, 1914.) Dr. Buckingham intimates in the first place (p. 356) that the theory of similitude contains nothing foreign to the ordinary theory of dimensions, and in the second place (p. 357) that all the consequences of the theory of similitude can be obtained from the principle of dimensional homogeneity. We shall show, however, that such is not the case.

etc., using a different arbitrary multiplier for each of the five fundamental properties, length, time, mass, permeability, and temperature.[1]

TABLE I.

Dimensions of a few Important Properties.[2]

Geometrical Properties.	**Dimensions.**
Length, l	$[l]$
Area, S	$[l^2]$
Volume, V	$[l^3]$
Angle, α	$[l^0]$
Kinematical Properties.	
Time, t	$[t]$
Velocity, v	$[lt^{-1}]$
Acceleration, a	$[lt^{-2}]$
Dynamical Properties.	
Mass, m	$[m]$
Density, ρ	$[ml^{-3}]$
Momentum, M	$[mlt^{-1}]$
Force, F	$[mlt^{-2}]$
Energy, U	$[ml^2t^{-2}]$
Energy Density, u	$[ml^{-1}t^{-2}]$
Pressure, p	$[ml^{-1}t^{-2}]$
Elasticity of compression, $E = V(dp/dV)$	$[ml^{-1}t^{-2}]$
Electrical Properties.	
Permeability, μ	$[\mu]$
Charge, e	$[m^{1/2}l^{1/2}\mu^{-1/2}]$
Inductivity, κ	$[l^{-2}t^2\mu^{-1}]$
Potential,	$[m^{1/2}l^{3/2}t^{-2}\mu^{1/2}]$
Capacity,	$[l^{-1}t^2\mu^{-1}]$
Current,	$[l^{1/2}m^{1/2}t^{-1}\mu^{-1/2}]$
Resistance,	$[lt^{-1}\mu]$
Electric field strength, E	$[l^{1/2}m^{1/2}t^{-2}\mu^{1/2}]$
Magnetic field strength, H	$[m^{1/2}]^{-1/2}t^{-1}\mu^{-1/2}]$
Thermal Properties.	
Temperature, T,	$[T]$
Entropy, S,	$[ml^2t^{-2}T^{-1}]$
Heat capacity,	$[ml^2t^{-2}T^{-1}]$
Specific heat,	$[l^2t^{-2}T^{-1}]$

In carrying out this multiplication, the values of derived properties will have to be multiplied by the proper combination of the arbitrary multi-

[1] For reference the dimensions of a number of important quantities are given in Table I. It was pointed out by Sir A. W. Rucker (Proc. Phys. Soc. Lond. (1888) 10, 37) that *five* fundamental properties are necessary for the treatment of our present body of physical knowledge, and the five used in the table are those most ordinarily chosen. In another place the writer will discuss a more rational choice of properties to be taken as fundamental.

[2] See any text on the dimensions of units, for example, Ency. Brit., 11th edit., article on "Units."

pliers x, y, z, etc., corresponding to the dimensions of the derived property in terms of those chosen as fundamental. It should also be specially noticed that if any dimensional constants occur in the equation, such as the R in the gas law $pv = NRT$ or the a in Stefan's law $u = aT^4$, these too will have to be multiplied by the suitable combination of x, y, z, etc., in order for the equation to maintain its invariance.

Method of Applying the Principle of Dimensional Homogeneity.—Let us now briefly consider the method of deducing physical laws from the principle of dimensional homogeneity so that we may later show the possibility of deriving laws from the principle of similitude that cannot be derived from the principle of dimensional homogeneity.

Considering equation (1), since all the terms in that equation must have the same dimensions, it is evident that if we divide through by $(-N')$ we shall obtain a new equation of the form

$$A + B + C + \cdots\cdots = 1, \tag{2}$$

where all the terms are now of zero dimensions. If now Q_1, Q_2, Q_3, etc., are quantities which express the values of the different properties whose quantitative interrelation is given by equation (2), each of the terms A, B, C, etc., will be some functional combination of these quantities. It is evident, moreover, that the only functional combinations of Q_1, Q_2, Q_3, etc., which will be of zero dimensions must be functions whose arguments are products of the general form

$$\pi = Q_1^{n_1}, Q_2^{n_2}, Q_3^{n_3}, \cdots, \tag{3}$$

where n_1, n_2, n_3, etc., are such integers that π itself is of zero dimensions. If now π_1, π_2, π_3, etc., are all the possible *independent* dimensionless products of this form, it is evident that we may rewrite equation (2) as follows

$$\phi(\pi_1, \pi_2, \pi_3 \cdots) = 1 \tag{4}$$

where ϕ may be any function.[1]

As a single illustration of the method of applying equation (4), suppose we wish to find the relation between the velocity of propagation v of a compressional wave in an elastic medium, the density of the medium ρ and its elasticity of compression $E = V(dp/dV)$. We have

$$[v] = [lt^{-1}], [\rho] = [ml^{-3}], [E] = [ml^{-1}t^{-2}]$$

and it is evident on inspection, that the only possible *independent* dimensionless product of these three quantities is $v^2(\rho/E)$ or some power of that combination. Substituting in equation (4) and solving for v we have a general expression for the velocity of a compressional wave

[1] This equation is equivalent to Dr. Buckingham's Equation No. 9, *loc. cit.*

$$v = k\sqrt{\frac{E}{\rho}}, \tag{5}$$

where k is the same constant for all different media. The simplicity of the calculation by which we have obtained this important equation of elasticity theory is evident.

Limitations of Dimensional Reasoning.—Dimensional reasoning is very attractive because of its great simplicity. Nevertheless, it is only fair to point out its serious limitations.

An important limitation to dimensional reasoning consists in the fact that the equations arrived at by such considerations always contain numerical constants, such as the k in our equation for the velocity of wave motion, and the values of these constants must be obtained from other than dimensional sources, for example by experiment. When the same equations are derived from the specific considerations of the particular theoretical field in question, the values of these constants are usually obtained in the course of the calculation.

In the second place, we must notice that in order to carry out dimensional reasoning at all, we must either know or assume just what are the physical properties which we shall expect to find connected by a physical equation. Thus, if we know or assume that the velocity of a compressional wave depends only on the density and compressibility of the elastic medium, it is possible to derive the correct equation as we have done above. Unless we knew beforehand, however, something about the field of investigation, we might expect that the velocity of the compressional wave to depend on other properties of the elastic medium as well, for example its rigidity, and could thus be led to incorrect results.

For us, however, the most important limitation to dimensional reasoning arises in cases where, without the introduction of a *dimensional constant*, no dimensionless product of the quantities involved is possible. A familiar example is provided by the equation connecting the pressure p, volume V, temperature T, and number of mols N of a perfect gas. The quantities involved are of the following dimensions $[p] = [ml^{-1}t^{-2}]$, $[V] = [l^3]$, $[T] = [T]$, and N the number of mols of gas may be looked upon as a pure number, which could be conceivable obtained by counting the number of molecules in the gas.

It is evident that there is no dimensionless product of these quantities since there is no way in which T can be cancelled out, and hence the principle of dimensional homogeneity will be of no assistance in predicting the form of the functional relation connecting them. The actual form of the familiar equation connecting the quantities is

$$pV = NRT \text{ or } \frac{pV}{NT} = R,$$

where R is the so-called gas constant. And in order that the equation shall agree with the principle of dimensional homogeneity we see that R must have the dimensions $[pV/NT]$, that is, of energy per mol per degree, *i. e.*, specific heat. Since, however, without a knowledge of the actual form of the equation there is no way to tell beforehand what the dimensions of such a constant would be, the principle of dimensional homogeneity is of no assistance in predicting the form of the equation. For example, if the gas laws were actually of the form,

$$\frac{p^3V^4}{NT^3} = \text{constant},$$

we should merely have to assign to that constant the dimensions $[p^3V^4N^{-1}T^{-3}]$ in order to agree with the theory of dimensions.

Another rather simpler example of the failure of dimensional reasoning to provide information as to the form of an important relation is furnished by the equation connecting the energy density u of a hohlraum and the temperature T. The dimensions of the quantities involved are

$$[u] = [ml^{-1}t^{-2}] \text{ and } [T] = [T],$$

and they permit of no dimensionless product. The actual relation between them is found to be

$$u = aT^4,$$

where a, the so-called Stefan's constant, must have the dimensions $[uT^{-4}]$ in order that the equation may agree with the principle of dimensional homogeneity. If the true relation, however, had turned out to be

$$u = aT^3$$

then a would have the dimensions $[uT^{-3}]$ and we see that dimensional reasoning gives us no assistance in predicting beforehand what the actual form of the relation is.

It is just in these cases where *dimensional constants* have to be introduced that the principle of similitude will sometimes come to our assistance, and permit a simple solution of problems that cannot be handled by ordinary dimensional reasoning. As we shall show, both of the examples considered above can be handled by the theory of similitude. In one case the theory provides a unique solution, and in the other prescribes important limitations to the actual form of the functional relation.

Let us now consider the content of the principle of similitude.

The Relativity of Size.—It is obvious that the numerical value obtained for the magnitude of any physical property which is capable of continuous variation will depend entirely on the magnitude of the unit chosen for the measurement. Thus the *numerical value* for the length of any object will be inversely proportional to the length chosen as a unit; the shorter we take our unit meter stick the more the number of times that we can fit it into the length of the object we are measuring.

Suppose now, however, that all objects in the universe should have their linear dimensions decreased in the ratio $1 : x$. Since the length of all our standards of measurement would be changed in the same ratio as all other lengths, it is evident that we should be unable to detect the change *by any ordinary process of measuring*, and this is what is meant by the idea of the relativity of size. When we speak of the length of a body, we really mean its length relative to some standard of measurement. If both the length of the body and the length of the standard of measurement should be suddenly changed in the same ratio, we should be unable to detect the change. Hence, we cannot speak of the *absolute* length of a body, but merely of the *relative* length of two bodies.

Although this principle of the relativity of lengths may seem very obvious it is not quite so simple as appears at first sight. This arises from the fact that there are other ways of estimating lengths besides that of counting the number of times the length of one object can be fitted into the length of another. For example, we might estimate the length of an object by noting the time it takes for a light signal to travel from one end of the object to the other. If now the length of our object were suddenly decreased, we should notice the fact since it would take a shorter time than before for light to travel from one end of the object to the other, *unless there should be a corresponding change either in the velocity with which light travels or in the rate of the clock which we are using to measure the time interval.* Now what we may call the idea of the *complete relativity of size* assumes the possibility of a coordinated change in the magnitudes of all measurable properties, lengths, time intervals, masses, temperatures, etc., of such a nature that no measurements of any description could lead to its detection. If such a coordinated change is possible, it will be meaningless to speak of the absolute size of any object in the universe.

The Principle of Similitude.—The idea of the *complete* relativity of size leads to the following statement of what may be called the principle of similitude: *The fundamental entities of which the physical universe is constructed are of such a nature that from them a miniature universe could*

be constructed exactly similar in every respect to the present universe.[1] This principle may be regarded, if wished, as a perfectly arbitrary postulate from which we shall deduce conclusions that may then be compared with the actual relations in the physical world.

The Transformation Equations.—Consider two observers O and O' provided with instruments for making physical measurements. O is provided with ordinary meter sticks, clocks, and measuring apparatus of the kind and size which we possess in our actual universe U. O', however, is provided with a shorter meter stick, and correspondingly altered clocks, standards of mass and other measuring apparatus so that he can make measurements in a miniature universe U', which, in accordance with the principle of similitude, is so constructed that he obtains the same numerical results in all his experiments as does O in the analogous measurements made in universe U.

We shall be most particularly interested now, not in the measurements which O and O' could make each in an entirely separate universe, but in the relation between the results which they obtain when each makes measurements of the same physical phenomenon.

Suppose, for example, O and O' both measure the length of the same object and obtain respectively the values l and l'. Then if O''s meter stick is shorter than O's in the ratio of $l : x$, the numerical value l' will obviously be greater than l in accordance with the equation

$$l' = xl.$$

In the first of the articles already referred to (loc. cit.) it was found possible to obtain a whole series of transformation equations of the type

[1] Ideas somewhat similar to that expressed by the principle of similitude have been considered in the past. Thus Newton, Lib. II., prop. 32, considers two similar dynamical systems, in which the particles are subjected to a *special law of attraction* and shows that if the two such systems are started with a similar configuration and state of motion, the particles will continue to move among themselves in each system with like motions and in proportional times; and Helmholtz, Jour. für Math., *97*, 319, 1884, has shown that for systems which obey Lagrange's equations of motion, corresponding to any state of motion, another state of motion could be obtained in which all the velocities are increased x-fold provided the external forces are increased by a factor x^2. There have also been a number of considerations on the basis of dimensional reasoning as to the corresponding behavior of animals or other physical systems which are similar in form, but of different size. The essential content of the principle of similitude, as stated above, seems to be entirely new, however, and we find, moreover, that the development of a complete theory of similitude is dependent on new ideas quite recently introduced into physics by the Einstein theory of the relativity of motion and by the electron theory, since the development makes use of the principle of the unalterable constancy of the velocity of light in free space and of the indivisibility and fundamentality of the charge of the electron as the natural unit quantum of electricity.

Note Added July 30, 1915.—The phrase principle of similitude has also recently been used by Rayleigh (Nature, March 18, page 67, 1915) to denote what I have called in accordance with common usage the principle of dimensional homogeneity.

TABLE II.

Transformation Equations.

Length,	$l' = xl$
Area,	$S' = x^2S$
Volume,	$V' = x^3V$
Time interval,	$t' = xt$
Frequency,	$\nu' = x^{-1}\mu$
Velocity,	$v' = v$
Acceleration,	$a' = x^{-1}a$
Mass,	$m' = x^{-1}m$
Density,	$\rho' = x^{-4}\rho$
Force,	$f' = x^{-2}f$
Pressure,	$p' = x^{-4}p$
Elasticity of compression,	$E' = x^{-4}E$
Energy,	$U' = x^{-1}U$
Energy density,	$u' = x^{-4}u$
Electrical charge,	$e' = e$
Entropy,	$S' = S$
Temperature,	$T' = x^{-1}T$

$l' = xl$, connecting the measurement made by O and O' of given lengths, time intervals, masses, forces, charges, etc., and in Table II. we present such a series of equations for future reference.[1]

[1] In deriving the transformation equation for absolute temperature, the writer inadvertently stated that absolute temperature had the same dimensions as energy. This is incorrect as was pointed out by Dr. Buckingham (*loc. cit.*). See, however, Lewis and Adams, PHYS. REV., III., 96, 1914, and Planck, "Vorlesungen über die Theorie der Wärmestrahlung." What the writer had in mind at the time was that since absolute temperature is proportional to the energy of the molecules of a monatomic perfect gas, the transformation equations for energy and for temperature must be the same. For example, consider the measurements of the temperature of a system which could be obtained by O and O' from observations of the mean kinetic energy of the molecules of a perfect gas which has been placed in thermal contact with the system in question. It is evident from the transformation equation for energy that these mean values of the kinetic energy will be connected by the relation $U' = x^{-1}U$ and hence since absolute temperature is proportional to the mean kinetic energy of such molecules our transformation equation for temperature must be

$$T' = x^{-1}T.$$

Another method of deriving the transformation equation for temperature would be to consider first the transformation equation for entropy. This is perhaps a more rational method of attack since we shall not need to consider the special properties of a perfect gas and shall hence feel more free to use our transformation equations in deriving the properties of a perfect gas.

Consider an *isolated* physical system which can exist in two different states (1) and (2). In accordance with the Boltzmann-Planck ideas as to the relation between entropy and probability we may write the equation

$$\Delta S = k \log \frac{W_2}{W_1}, \tag{1}$$

where ΔS is the increase in entropy when the system passes from state (1) to state (2), k is a universal constant and W_2/W_1 is the ratio of the respective probabilities of state (2) and state (1).

Method of Applying the Principle of Similitude.—The principle of similitude may be used to obtain information as to the form of the functional relation connecting the measurements of the properties of certain kinds of physical systems, namely, systems which might equally well form part either of universe U or of universe U' and would appear to have the same general nature in either universe. For such systems we may write the equation

$$F(Q_1, Q_2, Q_3, \cdots) = 0, \tag{6}$$

for the relation between the various measurements as made by O, or

$$F'(Q_1', Q_2', Q_3', \cdots) = 0, \tag{7}$$

for the relation between the measurements of the same properties as made by O'. Since, however, we are dealing with systems which have the same general nature in the two universes, it is evident from the

We may suppose that the quantities in equation (1) were measured by observer O. It is evident, however, that the system would also appear as a thermodynamic system to observer O' and hence his measurements would also have to obey the laws of thermodynamics in accordance with the equation.

$$\Delta S' = k' \log \frac{W_2'}{W_1'}. \tag{2}$$

It is evident from the principle of similitude, however, that the universal constant k' belonging to the miniature universe U' must be equal to the constant k in universe U. It is also obvious that W_2/W_1 is equal to the ratio which would be found by O for the relative lengths of time that the isolated system actually exists in states (2) and (1), while W_2'/W_1' is the same ratio as determined by O', which makes it evident that W_2/W_1 and W_2'/W_1' must be equal. We thus see that the quantities on the right hand sides of equations (1) and (2) are equal and hence obtain as the transformation equation for entropy

$$\Delta S' = \Delta S. \tag{3}$$

To obtain the transformation equation for temperature we may consider the equation

$$\Delta S = \int \frac{dQ}{T} \tag{4}$$

connecting the increase in entropy which accompanies a reversible change in the state of a system with the heat absorbed and the temperature of absorption. Since a reversible change in the state of a thermodynamic system would obviously appear to O' as well as to O to be reversible we may write for O''s observation of this same phenomenon

$$\Delta S' = \int \frac{dQ'}{T'}. \tag{5}$$

Now for $\Delta S'$ we may substitute ΔS in accordance with equation (3) and for dQ' which is a quantity of energy we may substitute $x^{-1}dQ$ in accordance with transformation equation for energy giving us

$$\Delta S = \int x^{-1} \frac{dQ}{T'},$$

and combining with (4) we have

$$\int x^{-1} \frac{dQ}{T'} = \int \frac{dQ}{T},$$

so that the transformation equation for temperature must be as we found before

$$T' = x^{-1}T.$$

principle of similitude that F and F' must be the same function, hence we shall be able to write

$$F(Q_1, Q_2, Q_3, \cdots) = F(Q_1', Q_2', Q_3', \cdots) = 0 \tag{8}$$

as a true equation. Our table of transformation equations, however, provides us with equations for all the Q''s in terms of the Q's, these equations being of the general form $Q' = x^n Q$. Substituting in (8) we obtain

$$F(Q_1, Q_2, Q_3, \cdots) = F(x^{n_1}Q_1, x^{n_2}Q_2, x^{n_3}Q_3, \cdots) = 0 \tag{9}$$

as an equation which will help us to determine the form of the functional relation F connecting the measurements of the various properties $Q_1Q_2 \cdots$ of the physical system in question. Since x is the ratio between the units of length in the two universes it can be any positive rational number, while the values for n_1n_2, etc., are either zero or whole numbers as given by our transformation equations. Under these conditions it is evident that we shall be able to obtain a *unique* solution for the form of F in equation (9) provided there are only two Q's (except for the particular case that n_1 and n_2 are zero). In case there are more than two Q's, equation (9) will not in general give a unique solution unless we have added information than that furnished by the principle of similitude; it will, however, often prescribe important limitations to the form of F.

We may now call particular attention to the fact that there is nothing to prevent the application of equation (9) to obtain relations which contain *dimensional constants* such as the R in the gas laws or the a in Stefan's law. We saw that the principle of dimensional homogeneity gave us no assistance in obtaining such relations because there is no way to know beforehand what the dimensions of these constants are going to be, and such knowledge is necessary in order to construct the dimensionless products which are the arguments of the desired functional relation (see equation 4). To use equation (9), however, no knowledge of these *dimensional constants* is necessary. They are quantities which in accordance with the principle of similitude must have the same magnitude in both universes U and U', and they do not occur among the measurements $Q_1, Q_2, Q_3, \cdots, Q_1', Q_2', Q_3', \cdots$ of those properties which have a different numerical magnitude depending on which observer measures them. The introduction of such dimensional constants in the final relation will occur because of the form of F and not because of its arguments.

A few simple examples of the application of the principle of similitude will make the foregoing analytical discussion clearer.

The Relation Between Mass and Energy.—The recent developments of physical science connected with the Einstein theory of relativity have

led us to expect a relation between the mass m and energy U of any system. If there is such a relation between the mass and energy of a system, it is evident that the principle of dimensional homogeneity will provide us with no information as to the form of the relation since there is no dimensionless product possible of $[m]$ and $[ml^2t^{-2}]$, so that the relation must contain a dimensional constant whose dimensions must be determined by other considerations. The principle of similitude, however, will permit a solution of the problem. We may write

$$m = F(U) \tag{10}$$

where F is the unknown function whose form is to be determined. If, however, there is a general relation connecting the mass and energy of any system, measurements made by O' on the same system which satisfy (10) would have to lead to the equation

$$m' = F(U'), \tag{11}$$

where in order to agree with the principle of similitude F has the same form as above.

Substituting our transformation equations for mass and energy and combining with (10) we obtain

$$m = x\, F\left(\frac{U}{x}\right) = F(U),$$

and since x may be any number the only solution for this functional equation is

$$m = kU, \tag{12}$$

where k is some constant. We have thus derived the important principle, familiar in the newer mechanics, that the mass of a system is proportional to its energy.

In order to make equation (12) agree with the principle of dimensional homogeneity it is evident that we shall have to assign to k the dimensions of the reciprocal of velocity squared, and as a matter of fact the constant has turned out to be the reciprocal of the square of the velocity of light.

The Relation between the Energy Density of a Hohlraum and the Temperature.—The energy density in a hohlraum at thermodynamic equilibrium is a function of the absolute temperature T. There is, however, no dimensionless product of $[u] = [ml^{-1}t^{-2}]$ and $[T]$, so that we cannot determine the form of the functional relation connecting the two quantities from dimensional considerations. We have, however, from the principle of similitude the equations

$$u = F(T),$$

and

$$u' = F(T'),$$

which would both be true since our system would obviously appear to both observers as a hohlraum at thermodynamic equilibrium. Substituting the transformation equations for u' and T' and combining we have

$$u = F(T) = x^4 F\left(\frac{T}{x}\right),$$

for which the only solution is

$$u = aT^4 \tag{13}$$

where a is a constant. We have thus derived Stefan's law from the principle of similitude, and having determined the form of the relation we now see that the constant a must have the dimensions $[ml^{-1}t^{-2}T^{-4}]$ to agree with dimensional considerations.

The Gas Laws.—There is a general relation connecting the pressure p, temperature T, volume v, and number of mols N of a perfect gas; there is, however, no dimensionless product of the quantities p, v, N and T, so that the principle of dimensional homogeneity will give us no assistance in determining the form of the relation. Let us suppose, however, an ideal gas composed of rigid elastic particles: such a system would evidently appear to both observers to be composed of rigid elastic particles, and hence would follow the same general laws in both universes. We may write

$$F(p, v, N, T) = 0 \tag{14}$$

for the measurements of O, and

$$F(p', v', N', T') = 0 \tag{15}$$

for the measurements of O', where, to accord with the principle of similitude, F must have the same form in both equations. Since N, the number of mols of gas in the system under consideration, could be determined by counting the number of molecules present, its value will appear the same both to observer O and O', and for the other quantities we have the transformation equations in Table II. Substituting in equation (15) and combining with (14) we obtain

$$F(p, v, N, T) = F(p', v', N', T') = F\left(\frac{p}{x^4}, x^3 v, N, \frac{T}{x}\right) = 0.$$

There is no unique solution for this equation. If, however, we assume Boyle's Law that the pressure volume product is a constant at a given temperature, and Avagadro's hypothesis which makes the pressure volume product proportional to the number of mols of gas, we may rewrite our equation in the form

$$F_1\left(\frac{pv}{N}, T\right) = F_1\left(\frac{p'v'}{N'}, T'\right) = F_1\left(\frac{pv}{xN}, \frac{T}{x}\right) = 0,$$

and the only solution of this equation is in the form

$$\frac{pv}{NT} = R, \quad pv = NRT,$$

where R is a constant. Given the principles of Boyle and Avogadro, we have thus derived the Law of Charles from the principle of similitude. To agree with dimensional considerations R must have the dimensions of heat capacity per mol.

Other applications of the principle of similitude will be found in the articles already referred to; see also an article by G. Nordström[1] for a discussion of the intimate relation between the principle of similitude and his theory of gravitation.

Limitations of the Principle of Similitude.—There are limitations to the application of the principle of similitude to some extent similar to those found in dimensional reasoning. In the first place, just as in the case of dimensional reasoning, we obtain from such considerations no information as to the magnitude of the constants which are introduced into our equations, while a derivation of the same relations from the considerations of the special field in question usually provides such information.

It should also be noticed that just as in dimensional reasoning we have to know or assume *just what are the quantities* which we shall expect to find connected by a physical equation. If we leave out some quantity which belongs in our relation, we shall deprive our functional equation of a necessary multiplier, of the form x^n, and shall thus obtain an incorrect result. Similar considerations would apply to the introduction of an unnecessary quantity.

We must also call attention to the fact that we must necessarily restrict our application of the principle of similitude to systems which could form equally well a part of universe U or universe U', and whose properties would be connected by the same functional relation in both universes. It is a little difficult to be quite sure as to the actual significance and scope of this restriction. It is perhaps identical with the fact that in order to apply the principle of similitude we must be sure to introduce all the physical quantities which are necessary to the complete physical equation.

Relation of the Principles of Dimensional Homogeneity and of Similitude.

[1] Öfversigt af Finska Vetenskaps-Societens Förhandlingar, Bd. *58* (1914–15), Afd. A, No. 22.

—In conclusion it will now be possible to state the principles of dimensional homogeneity and of similitude in such a form as to make their relation and difference quite evident. As we have already seen the principle of dimensional homogeneity requires that all the essential equations of physics shall be unaltered if we substitute for every length in the equation a value x times as great, for every interval of time a value y times as great, for every mass a value z times as great, and so on for all the fundamental properties. For measurements of derived properties which enter the equation we must substitute their value multiplied by the appropriate combination of x, y, z, etc., which is obvious from their dimensions. It should be particularly noticed, however, that this invariance will not obtain in those equations which contain constants like the R of the gas laws or the a of Stefan's law, unless indeed we assign suitable dimensions to these constants.

In comparison with the above requirement, the principle of similitude requires that the equations to which it applies,[1] shall remain invariant when the various measurements are multiplied not by a combination of different multipliers x, y, z, etc., one for each fundamental property, but when they are multiplied by different powers of the one quantity x as given in the table of transformation equations. Moreover, the quantities which have to be so multiplied in order to obtain invariance include only those actually measured, and not any of the so-called dimensional constants.

These parallel statements will make the relation of the two principles evident. Where dimensional constants enter, the principle of dimensional homogeneity is of no avail in predicting the form of a relation, since we cannot tell beforehand what the dimensions of the constant are going to be. For such problems we must have recourse to the principle of similitude. On the other hand, when dimensional constants do not enter into the relation, although we may apply either principle, the principle of similitude is usually the less powerful since it merely prescribes invariance when the different measurements are multiplied by powers of a single arbitrary multiplier x, while the principle of dimensional homogeneity prescribes the more drastic requirement of invariance when the multiplications are carried out with a different arbitrary multiplier for each fundamental property.

As an example of the greater power of the principle of dimensional homogeneity in a case where both principles are applicable, we may consider again the relation between the velocity v of a compressional wave

[1] *I. e.*, equations connecting the properties of systems capable of forming part either of U or U'.

and the density ρ and elasticity E of the liquid. We have from our table of dimensions

$$[v] = [lt^{-1}],\ [\rho] = [ml^{-3}],\ [E] = [ml^{-1}t^{-2}],$$

and see that the only *independent* dimensional product is of the form $v^2(\rho/E)$ and hence that our relation must be of the form

$$v = k\sqrt{\frac{E}{\rho}}.$$

If we apply the principle of similitude to the same problem we obtain

$$v = F(\rho, E),$$
$$v' = F(\rho', E'),$$

or substituting our transformation equations and combining

$$v = F(\rho, E) = F\left(\frac{\rho}{x^4}, \frac{E}{x^4}\right),$$

which has no unique solution but prescribes

$$v = F_1\frac{E}{\rho},$$

as a necessary form of the final relation. We see that in this case the principle of similitude leads to a correct result but does not provide such explicit information as the principle of dimensional homogeneity.[1]

[1] These considerations might indicate that in those cases where both can be applied it is usually better to use the principle of dimensional homogeneity than the principle of similitude. Nevertheless, even in such cases there is sometimes an advantage from the point of view of simplicity and fundamentality in employing the principle of similitude instead of dimensional reasoning. Thus there are a number of electrical problems, in particular problems concerning the properties of the electron, which were treated by the author in his first paper, *loc. cit.* Buckingham has shown (*loc. cit.*) that these same problems, although perhaps with less ease and directness, can be treated by dimensional methods. To do so, however, he has had to introduce the electric inductivity and magnetic permeability of the medium in which the electron in question is situated and take account of the dimensions of inductivity and permeability. From the point of view, however, of modern electromagnetic theory as developed by Lorentz, the inductivity and permeability of a medium is in the nature of a statistical result of the activities of individual electrons, and each actual electron is itself situated in *free space*. For this reason there are some advantages in treating such problems from the point of view of the principle of similitude.

UNIVERSITY OF CALIFORNIA,
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PROCEEDINGS

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MECHANICAL STRAIN AND THERMOELECTRIC POWER.[1]

BY WALTER P. WHITE.

1. The emphasis generally and justly laid upon the importance of exact measurement has had one unfortunate consequence, in that phenomena, even though important, which do not lend themselves easily to measurement are apt to suffer a comparative neglect. Such is the case with some of the results of permanent mechanical strain in metals. It is difficult to specify definitely either the amount or character of the changes due to such strain; it is even uncertain what they consist in, and yet their effect upon the thermoelectric power may throw light upon the important and obscure questions which exist regarding the relations of electricity to metals. A few observations upon this effect are therefore given here.

2. In general, the effect of alloying a metal is to lower the thermoelectric power. The effect of hardening by permanent strain (bending, drawing through dies, etc.) either a pure metal or an alloy is to *raise* the power. Hence hardening has an opposite effect to alloying, though of less amount. Platinum alloys, however, are most of them higher than platinum. And the alloy of platinum containing 10 per cent. of rhodium (and probably other platinum alloys also) is lowered by mechanical hardening, so that here also alloying and hardening have effects opposite to each other. Pure platinum, however, is changed in the same direction by hardening and (usually) by alloying.

One probable result of this opposite behavior of pure platinum and its alloys is that there are alloys of such compositions that hardening has no effect on their thermoelectric power. And it is possible, also, that this result might be strictly true for one sort or method of hardening, but not for others, so that various methods would cause an alloy of the proper composition to vary in opposite ways. If this is so, it opens up a new line of investigation upon the character and effects of permanent strain.

The platinum metals, on account of their freedom from oxidation, and the consequent ease of annealing, are very well adapted for investigations of this character.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

3. The thermoelectric effects of temporary strain (strain below the elastic limit) have no perceptible relation to those due to permanent strain, or hardening. Hydrostatic pressure raises the thermoelectric power in metals and alloys, though with some exceptions, of which manganin is one. But I found that tension lowered the thermoelectric power for platinum, platinum-rhodium, copper, and constantan, and raised it for manganin. The magnitude of the effect was very roughly the same for copper as with pressure (6×10^{-6} microvolts per degree per kg./sq. cm. against 3×10^{-6} quoted by Baedeker for pressure), was more for platinum, less for manganin and constantan. It will be noticed that *temporary* strain affects platinum-rhodium like platinum and most other metals. Both platinum and its alloy showed nearly or quite an identical effect from tension when hard and when annealed, but the alloy gave less than half as much as platinum.

4. A certain sample of constantan wire, hardened by drawing from 2.5 to .25 mm. diameter, was softened by careful annealing near 800°. Another portion of the same, annealed near 300°, remained mechanically rather hard, but was as soft, *i. e.*, as low, thermoelectrically, as the other. *A metal, therefore, may be in a state of relative mechanical hardness without possessing the corresponding thermoelectric condition.* The same effect has been observed with platinum, which is generally annealed perfectly at a dull red heat, though not then so soft mechanically as after a heating to 1300° or so. In one instance, however, the thermoelectric power was lowered by a high heat after it had become apparently constant by heating to a dull red.

5. Even in a short and simple communication upon thermoelectricity, it seems necessary at the present time to specify what convention is used regarding the sign of the thermoelectric power. The best authorized notation, used from the discovery of thermoelectricity in 1821, and sanctioned by the leading texts and collections of tables in English, French, and German (with the exception of Mascart and Joubert) defines that metal as positive from which the current flows at the cold junction. This makes antimony, iron, copper, and platinum-rhodium positive to platinum, mercury, nickel, constantan, and bismuth.

The opposite notation has, however, been used in some cases, upon what grounds I have been unable to learn, but with the result of causing much confusion. Thus A. L. Bernoulli published in 1910 a theory of thermoelectricity[1] which, on account, as he explains, of this confusion of signs, gave results directly opposite to observation, and therefore had to be modified so as to reverse the sign of the results predicted—a feat which he promptly and successfully accomplished.[1] Even so, however, he still suffered from the confusion apparently, for he takes the platinum rhodium alloy to be negative towards platinum, and finds that this is in accord with his second theory, whereas this alloy is really positive. At about the same time Koenigsberger,

[1] Ann. Physik, 33, 690.

[2] Verh. d. Phys. Gesell., 1911, 213.

who used the unauthorized system of signs, was thereby deceived into thinking that he had obtained the same value for silicon as Wick, whose signs were correct. Again, the last (1914) edition of the Smithsonian Tables gives thermoelectric power in different ways on different pages. This contradiction is soon to be corrected in a new issue.

In this abstract the authorized convention as to sign has been followed.

NEW BOOKS.

Unit Photography. F. M. Steadman. New York: D. Van Nostrand Co., 1914. Pp. xi + 160. Price, $2.00.

The purpose of the book announced in the introduction is a desire to establish a rational scientific foundation for the practice of photography. The author proceeds first to demonstrate the fact that such a foundation is lacking at the present time. Those who have had practical experience in photography, even as amateurs, need very little persuasion or argument to convince them of the justification of this conclusion. The bewildering confusion of lens speed, diaphragm opening, sensitometer number, emulsion number, season of year, time of day, state of the weather, character of the subject and finally the all important question of length of exposure necessary to secure a satisfactory negative which confronts all beginners and the great majority of somewhat experienced workers is too well realized to require any special emphasis. The reviewer has dabbled in amateur photography from time to time for a period of nearly thirty-five years and has been constantly impressed by the utter lack of any real systematic progress in the scientific aspects of the subject. Although there has been an enormous increase in the manufacture and use of photographic apparatus, and although a great number of people have cameras of one sort or another and use them occasionally, the available rules for operating have retained their primitive simplicity and uncertainty. The one fundamental essential of satisfactory photographic work is the securing of a correct, initial exposure and the necessary requirements for obtaining this are the ones which have received the least systematic and intelligent consideration up to the present. In the opinion of the author, "a perfect exposure is one which creates in an emulsion a latent image which may be developed under known conditions and without special attention, into exactly the character of negative which the worker in that particular case desired to obtain."

The book is written with the object of providing a practical method for determining the proper exposure from a study of the light values of the subject, the size of the diaphragm opening and the speed of the emulsion. Discussing the question of the light values of the subject the author makes use of the expressions "actinism" and "actinity." The latter is defined as "the capability of radiation to produce certain chemical changes on converging at a point." The general bearing of these factors on the chemical action produced in the emulsion is discussed and explained. The importance of the solid angle subtended by a given object is emphasized as being one of the elements requiring

consideration. The author describes a simple and apparently practical device which is to be used as an actinometer and a considerable number of practical problems in actinometry are stated and solved in illustrating the manner in which the apparatus is employed. The subjects subsequently treated include the comparison of different actinicities, the classification of the subjects to be photographed, the Hurter and Driffield system and the general topic of negative making. The important element of the latitude and endurance of emulsions and the bearing of these on the nature of the subject and the time of exposure are discussed in a very enlightening manner.

The reader of this book can not avoid being impressed by the sane and practical treatment which the subject has received in the hands of the author. The book contains a good deal of valuable information and affords intelligent answers to many of the questions which have long perplexed the average photographer. It is perhaps unfortunate that the plates, of which there are thirteen given, do not possess greater artistic merit, although from the standpoint of photographic technique they are in all respects satisfactory.

B. B. BOLTWOOD.

Optic Projection. By S. H. GAGE and H. P. GAGE. Ithaca: Comstock Publishing Co., 1914. Price, $3.00.

While this manual is written especially from the standpoint of the user of projection apparatus and of the manufacturer, it is thorough and scientific, and the physicist will find in it a clear exposition of the principles involved. First the use of the magic lantern with different methods of illumination is taken up in detail, then micro-projection, and motion picture apparatus, concluding with the optics of projection and its application in physics and in the study of vision.

Detailed instructions and practical hints are given throughout. The book shows intimate knowledge of the most modern apparatus derived from close contact with the manufacturer, and this knowledge is presented clearly and compactly by the constant use of excellent plates and diagrams. An interesting historical sketch is given as an appendix, with a list of manufacturers, and a complete bibliography. Altogether the book deserves praise, and makes a valuable addition to the literature on projection.

P. V. W.